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7/25/68

THE SORPTION OF TEXTILE DYES BY ACTIVATED CARBON

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

Chadwick Perrin Smith

In Partial Fulfillment

of the Requirements for the Degree

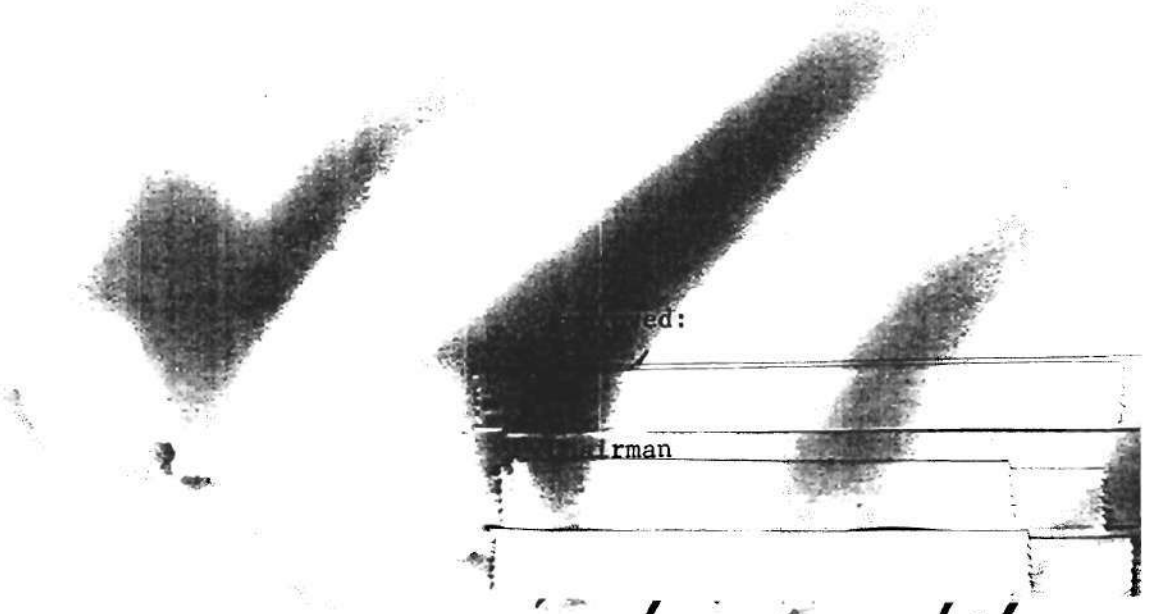
Master of Science in the School of Textiles

Georgia Institute of Technology

December, 1971

THE SORPTION OF TEXTILE DYES

BY ACTIVATED CARBON



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Date approved by Chairman: Nov. 29, 197

ACKNOWLEDGMENTS

I would like to express my appreciation to my thesis advisor, Dr. Walter C. Carter, for the guidance and the many hours of his time which he contributed.

I am grateful to Dr. James L. Taylor, Director of the School of Textiles, for his efforts in providing the opportunity and securing the financing which made my attendance of graduate school possible.

Dr. Billy H. Kornegay and Dr. Wayne C. Tincher served as members of my reading committee and provided valuable advice, and I greatly appreciate their help.

I am grateful to Mr. A. W. Loven, Manager of Carbon Development for Westvaco, for generously providing the activated carbon and accompanying data.

I would like to express my gratitude to the Tennessee Eastman Company for providing the fellowship which made the completion of this thesis and my graduate education possible.

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SUMMARY

Tertiary treatment is often necessary to effectively remove color from textile dyehouse wastewaters. Adsorption with activated carbon is an economically feasible method of tertiary treatment, and it has already been applied to the treatment of some dyehouse wastes. The variable nature of dyehouse wastes causes the effectiveness of the carbon in treating these wastes to vary.

The purpose of this work was to evaluate the effects of variations in dye molecular structure, temperature, and pH on the adsorption of dyes with anthraquinone structures from water by activated carbon. The effects of the presence of an inorganic electrolyte and of a surfactant in solution on the adsorption of dye from water was also examined.

It was concluded that the addition of a second sulfonic acid group to a monosulfonated anthraquinone dye decreased the equilibrium adsorption of the dye from water. Increased temperature increased the rate of adsorption, and in one case, the equilibrium adsorption of dye. A decrease in pH increased the equilibrium adsorption of anthraquinone dyes with sulfonic acid groups. The presence of a large concentration of sodium sulfate in solution increased the equilibrium adsorption of sulfonated anthraquinone dyes, and the presence of an anionic surfactant decreased the adsorption of these dyes.

CHAPTER I

INTRODUCTION

Statement of the Problem

It has been estimated that ten million pounds of dyestuffs are discharged annually in the wastewaters of textile dyeing operations (1). The highly colored nature of these wastes makes them particularly objectionable pollutants of rivers and streams. The portion of these wastewaters which receives some treatment for the removal of pollutants before being expelled into natural bodies of water is usually subjected to a biological treatment (2). However, some types of dye have been shown to be resistant to biological degradation. Among these resistant types are the dyes whose chemical structures are modifications of the anthraquinone structure (3). Even the dyes which are degraded may yield degradation products which are more harmful to the environment than the dyes themselves (4). New dyes are constantly being developed with improved resistance to degradation when in textile products, and consequently, they are move resistant to biological treatment in wastewaters. Wastewater treatment processes which remove these dyes from solution rather than attempt to degrade them in solution are needed.

Adsorption of dye wastes on activated carbon has been shown to be effective and low in cost compared to most other methods for tertiary waste treatment (1). Several operations involving activated carbon for the removal of dyes from the wastewater of dyeing plants have already

been placed into service (4,5).

Water from typical dyeing operations contains many materials in addition to dye. Suspended solids, dyeing auxiliaries and assistants, salts, acids and alkalies, softeners, water repellants, and detergents or soaps may be present along with other impurities (6). The presence of these additives as well as variations in temperature and pH of textile dye wastewaters may affect the rate and capacity for the adsorption of a particular dye by activated charcoal. The structural variations between molecules of different dyes would also be a factor in the amount of color removed from solution by an activated carbon. The composition and character of dye wastes are varied. There is a scarcity of information about removing color from particular types of dye wastes, and this is a handicap to companies trying to find solutions to dye waste problems (2).

The purpose of this work is to provide additional information on the effect of the chemical structure of the dye, pH variation, temperature variation, and the presence of some chemicals typical of those found in dyeing and finishing operations on the equilibrium adsorption of color from solution onto an activated carbon designed and manufactured for the removal of colored materials from solution. The dyes under consideration are members of the biologically resistant anthraquinone family, and the particular variation in chemical structure examined will be a variation in the number of sulfonic acid groups on the same basic dye structure. It is expected that this work will be of benefit to those who are concerned with particular types of dye wastes.

Review of the Literature

Work with Dyes

Dyes have frequently been used in studies on adsorption by activated charcoal. Their concentrations in solution can be determined colorimetrically and the amounts adsorbed from solution easily calculated. Freundlich and Losev (7) examined the adsorption of dyes from solution onto activated carbon and found that an equilibrium was established which could be accurately represented by the equation:

$$X/M = AC^{1/p}$$

In this equation X/M represents the amount of dye adsorbed at equilibrium per unit weight of carbon. C is the concentration of dye in solution which is in equilibrium with the dye on the carbon. A and 1/p are constants which may be obtained from a full logarithmic plot of X/M versus C. The Langmuir and Brunauer-Emmett-Teller equations are also used to describe adsorption equilibrium states, but the Freundlich equation is often found satisfactory in describing adsorption equilibria in solution, and it is frequently used (8).

Effect of Molecular Structure and Chemical Groups. Knecht (9) examined the adsorption of Crystal Scarlet (Color Index Number 16250), a disulfonated acid dye, and Methylene Blue (CI 52015), a basic dye whose structure and chemically active groups are markedly different from Crystal Scarlet, on activated carbon which had been treated to reduce the nitrogen content. This reduction in nirogen content reduced the adsorption of Crystal Scarlet but had little effect on the Methylene Blue adsorption. Knecht concluded that dyes with different structures

and chemically active groups are adsorbed by different mechanisms and in different amounts by activated carbon.

Rohland (10) studied the adsorption of eight dyes on animal charcoal. The dyes varied widely in chemical structure but one trend was evident-dyes containing basic groups were generally adsorbed more rapidly than dyes whose chemistry was dominated by sulfonic or carboxylic acid groups in the dye molecule. Pore size distribution in the carbon and the variation in molecular size of dyes could have been a factor in determining the order of adsorption in some cases.

Graham (11) has done work on the adsorption of Methylene Blue and Metanil Yellow (CI 13065) by six different activated carbons. Although similar in molecular size, Methylene Blue is basic in character, while Metanil Yellow contains a sulfonic acid group. Graham concluded that acidic groups on the carbon surfaces which give a net negative charge to the carbon surface in solution hamper the adsorption of Metanil Yellow relative to Methylene Blue. Molecular size was not a major factor since the two molecules are similar in size.

Rodman (2) described work in which aqueous solutions of dyes of four types were subjected to treatment in granulated activated carbon columns. Direct Blue 106 (CI 51300), Acid Black 26A (CI 27075), Reactive Red 3, and Disperse Blue 3 (CI 61505) were the dyes used. Each dye was examined in solution with chemicals commonly used in conjunction with its application to textile materials. At constant temperature and flow rate the amount of color remaining in the effluent from the columns was measured at regular time intervals. The results obtained indicated something of the rate and equilibrium adsorption for the four dyes.

Disperse Blue 3, which has an anthraquinone structure with no groups strongly polar enough to give the dye more than an extremely small solubility in water, was poorly adsorbed by the carbon. It was conjectured that only the small amount of the dye which was in solution was adsorbed onto the carbon, and that the majority of the dye which was in suspension was not adsorbed. The direct and acid dyes which each contained two sulfonic acid groups and were of roughly the same molecular size showed a similar degree of adsorption which was considerably greater than that of the disperse dye. The reactive dye was adsorbed to the greatest extent but its exact structure was not known.

The Effect of pH. The effects of pH variation on adsorption of dyes by activated charcoal have been reported by several investigators. Yajnik et al. (12) observed that the basic dyes Methylene Blue and Bismarck Brown (CI 21000 or 21010) were adsorbed less as the pH was lowered, and that Water Blue (CI 42755) which contains three sulfonic acid groups was adsorbed to a greater extent with a lowering of pH. Sastri (13) reported that Methylene Blue was adsorbed in lowest amount from a solution with a pH in the isoelectric zone for Methylene Blue (pH 3.75 - 3.97). Grollman's investigations (14) of the adsorption of a disulfonated direct dye called Phenol Red (CI 27680) on blood charcoal indicate that adsorption gradually decreases from pH 1.5 to pH 6, and then rapidly drops between pH 6 and pH 10. The work of Miller and Bartell (15) on the adsorption of the basic dyes Methylene Blue and Crystal Violet (CI 42555) and the acid dye Eosin (CI 45380) which has a carboxylic acid group revealed that these dyes were adsorbed to a certain extent by hydrolytic means in which the basic dyes were con-

verted to the free base and the acid dye to a free acid in the adsorption process. pH changes which promote the conversion to free bases or acids would promote adsorption. Doss and Singh (16) report the adsorption of Thymol Blue, a dye with at least one sulfonic acid group, decreases as the pH is raised from 1.2 to 10.0.

Effect of Strong Inorganic Electrolytes. The effect of electrolytes on the adsorption of dyes has been investigated. Hassler (17) examines work done on Methylene Blue, Crystal Violet (CI 42555), and Auramine (CI 41000) in solution with various inorganic salts. The presence of salt increased adsorption. The salts containing sulfate or chloride anions were consistently the most effective in promoting increased adsorption of dye. Pincussen (18) did work on the adsorption of Methylene Blue from solutions containing inorganic salts. The adsorption of Methylene Blue was increased by the presence of sodium chloride for each of the four carbons tested. Sodium sulfate gave an increase in adsorption of dye on two of the carbons and a decrease on the other two.

Effect of Temperature. The temperature effect on adsorption from water by activated carbon of a series of dyes encompassing several acid and basic dyes of various structures was observed by Rossi and Basini (19). An increase in temperature caused an increase in the amounts of dyes adsorbed, with different dyes showing different magnitudes of increase. Siegrist and Pelet-Jolivet (20) reported that adsorption on charcoal was increased with increased temperature for solutions of Methylene Blue and Crystal Ponceau (CI 16250) which is a trisulfonated acid dye. Hassler (17) reports that basic dyes Methylene

Blue and Malachite Green (CI 42000) are adsorbed more from solutions on each of three activated charcoals at 80°C than at 20°C. An anthraquinone dye with a sulfonic acid group, Alizarin Red (CI 58005), showed increased adsorption at the higher temperature for two of the carbons and decreased adsorption at 80°C for the third.

Effects of Solvent. The effects of different solvents on the adsorption equilibria of dyes on activated carbon is of interest, since two different solvents are used in this work. Hassler and McMinn (21) examined the adsorption of Methylene Blue, Malachite Green, and Alizarin Red from water and from ethanol onto activated carbon. All of the dyes were adsorbed less from alcohol and it is suggested that the affinity of carbon for alcohol is greater than that of carbon for water. The result is that more solvent is adsorbed when alcohol is the solvent. Also, the attractive forces between solute and solvent are altered by changing the solvent, and this affects adsorption. The relative order of the magnitudes in which the three dyes are adsorbed from water and ethanol differs, showing that the solvent has considerable effect on the mechanism of adsorption from solution.

Work on Substances Other than Dyes

No work was found in the literature which deals with the effect of other adsorbable organic compounds in a dye solution on the adsorption of dye. Works were found describing the competition between two different organic substances for adsorption onto activated carbon from the same solution. Weber and Morris (22) report that solutions containing sodium (2 - dodecyl)benzenesulfonate and phenol in water show a decrease in both rate and equilibrium adsorption for each compound

compared to that for either compound alone in aqueous solution. However, at equilibrium the carbon absorbs more material from the solution with mixed solutes than it does from solutions containing either one of the components singly. Goddard and Cooper (23) examined the adsorption of several benzoic acid derivatives from solution onto activated carbon. The presence of formamide or 1, 4-dioxane in solution with the benzoic acids decreased the amount of acid adsorbed in every case.

General Observations

Several authors have made general observations on the influence of solute molecular structure, pH, temperature, and electrolyte content on the adsorption by activated carbon from solution.

Effect of Structure and Chemical Groups. Hassler (17) has stated that specific groups on an adsorbed molecule influence the orientation of that molecule on the carbon surface, and therefore, the number of molecules which may be adsorbed on the surface. He states that the introduction of a sulfonic acid group usually decreases the adsorbability of that molecule from aqueous solution and that the introduction of a second identical group often enhances the action of the first. Increased solubility of the solute, reflecting a greater affinity between the solvent and solute, may be the main cause of this reduced adsorption.

Effect of pH. Porter (24) states that pH may affect the adsorption of solutes by altering the ionic charge on a solute and by changing the carbon surface. Hassler (17) reports that adsorption from aqueous solution is usually increased by conditions which reduce the ionization of a solute. This can affect both the rate and equilibrium

capacity, and would mean that salts in which the acid component is the adsorbable portion would show increased adsorption from a medium of low pH. The reverse would be true with a salt in which the base was the adsorbable portion. Hassler also states that the effects of pH on the carbon are small compared to the effects on the solute. Getzen and Ward (25) report that generally the adsorption by activated carbon of weak electrolytes from aqueous solution takes place in such a way that the undissociated molecule is preferred rather than the ionized form, and that pH versus adsorption curves generally parallel dissociation curves for a weak electrolyte.

Effect of Temperature. Increased temperature decreases the viscosity of a solution, steps up diffusion of a solute into a carbon particle, and aids in the removal of preadsorbed gases from the carbon (17). The result is a more rapid rate of adsorption. Temperature increases may affect the equilibrium adsorption but it is difficult to predict the magnitude or direction of the effect. In cases where Van der Waal's forces are the only mode of adsorption, the temperature increase generally decreases the equilibrium capacity of carbon. In cases where adsorption forces are due to a chemical interaction between carbon and solute stronger than Van der Waal's forces, the temperature effect is difficult to predict. Higher temperatures may initiate bonding of an order higher than Van der Waal's forces.

Effect of Strong Inorganic Electrolytes. The influence of salt on adsorption is specific depending on the relation between the chemical natures of the salt and the substance to be adsorbed (17). Usually a strong inorganic electrolyte will not compete with other solutes for

adsorption onto activated carbon (17). Electrolytes may serve to neutralize the charge built up on the carbon when an ionic solute is adsorbed onto the carbon, and in this manner increase adsorption rate and equilibrium capacity (24).

Summary

From this survey of the literature it is obvious that the adsorption of dyes from solution by activated carbon has been extensively examined. The effects on adsorption of various chemically active groups on the dye molecule can be observed from the literature. However, the specific effects of these groups have frequently been masked by variations in other aspects of molecular structure and variations in the molecular size of dyes used to compare the effects of different chemically active groups. The information on the effect of pH variation on adsorption makes the direction of the effect predictable, but not the magnitude. For the dyes reviewed in this literature survey, a rise in temperature is generally seen to increase adsorption but not in all cases. The salt effect is specific for the particular system. No work has been found which measures the effect of other organic substances in a dye solution on the adsorption of dye. Little work has been found to concentrate on the biologically resistant anthraquinone dyes, since only two of the dyes mentioned in the literature surveyed were of this type.

The intent of this work is to provide further knowledge about the effects of certain variables on the absorption of dyes with a particular basic structure which have been shown to be resistant to biological attack. Effects of the addition of sulfonic acid groups to almost identical anthraquinone type structures will give a clear indication of the

effects of these groups without consideration of variance in basic dye structure or wide variations in molecular size. The magnitude of pH effects on adsorption for this little studied class of dyes will be measured, as well as the particular effects of salt and temperature on the adsorption. The effect of a second organic substance in solution should be of interest, since no work has been found on this subject in relation to dyes.

Perhaps this work will provide useful information to those working on specific dye waste control problems.

CHAPTER II

INSTRUMENTATION, EQUIPMENT, AND CHEMICALS

The constant temperature bath used in this work consisted of a glass tank filled with polyethylene glycol. Temperature control was achieved by the use of a Fisher Unitized Bath Control which included a heater and thermoregulator. Temperature was monitored by means of a thermometer whose calibration had been checked in an ice water bath. A constant source of heat was provided by a 750 watt flexible immersion heater regulated with a 120 volt Staco Variable Autotransformer (type 2PF1010). A copper coil connected to a cold water source was placed in the bath to facilitate cooling of the bath. A Palo-Myers 110 volt stirrer was used to insure a uniform temperature throughout the bath. The bath temperature was controlled to $\pm$ 0.2 C.

Flasks containing test solutions were agitated in the bath by means of a Burrell Wrist Action Shaker.

Filtration of dye solutions was accomplished using two Gelman filtering devices attached in series to a vacuum flask and vacuum line. Gelman glass fiber filters (type A, 47 millimeters in diameter) were used in the filtering devices.

Dye solutions were analyzed using a Beckman Model DB-6 Grating Spectrophotometer equipped with scanner, ten inch recorder, and one centimeter silica cells.

All weighings were made on a Mettler H6T analytical balance. The

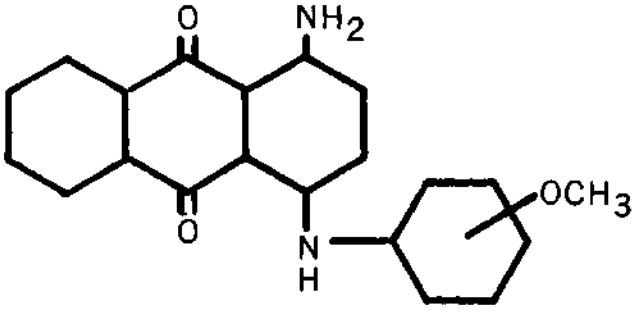
pH readings were made on a Corning Model 10 pH meter.

Reagent grade anhydrous sodium carbonate, sulfuric acid, xylene, methanol, and N,N-dimethyl formamide were obtained from the Fisher Scientific Company. The reagent grade pentane used in dye purifications was obtained from the Matheson Coleman and Bell Company. Reagent grade anhydrous sodium sulfate and monohydrated sodium phosphate were obtained from the J. T. Baker Chemical Company. The anhydrous disodium phosphate was obtained from the Monsanto Chemical Company. The surfactant, Igepon T, which contained 28 percent by weight of the active ingredient sodium N-methyl N-oleoyl taurate was supplied by the General Aniline and Film Company.

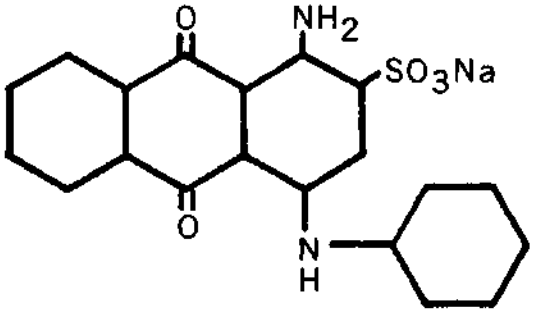
Water for use in this work was distilled in an all glass still.

The dyes, Disperse Blue 9 and Acid Blue 25 were obtained from Geigy Dyestuffs Company. Commercial names for these dyes are Cibacete Blue RAF and Erio Fast Blue GRL respectively. The dye, Acid Blue 145, was supplied as Anthraquinone Blue 3G by the E. I. DuPont de Nemours Company. The molecular structures of the dyes are shown in Figure 1.

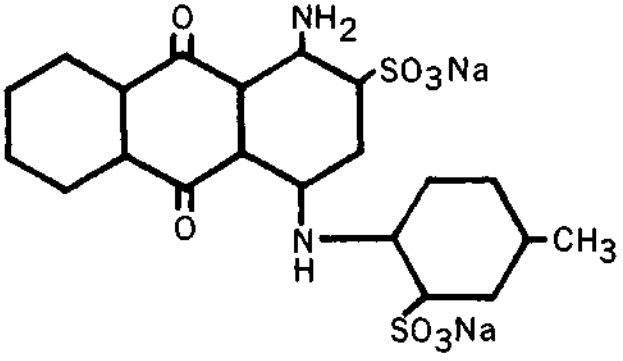
Granular activated carbon, Nuchar WV-L, was supplied by Westvaco. Data on the carbon may be found in Appendix A. The granular form of carbon was used in preference to the powdered form because of ease of handling and filtration.



DISPERSE BLUE 9 (CI 61115)
Molecular Weight - 344.4



ACID BLUE 25 (CI 62055)
Molecular Weight - 416.4



ACID BLUE 145 (CI 62070)
Molecular Weight - 532.5

Figure 1. Molecular Structures of Dyes

CHAPTER III

EXPERIMENTAL PROCEDURES

Analysis of Dye Solutions

The relationship between absorbance and concentration was studied for the dyes in the various types of solutions which were to be used in adsorption experiments, so that the concentrations of solutions after contact with carbon could be calculated. Solutions of known dye concentration were prepared and examined spectrophotometrically. The reference cell of the spectrophotometer contained a solution identical to that in which the dye was dissolved, so that any effect of added chemicals other than dyes on the absorbance was negated. Absorbances between the wavelengths of 700 and 400 nanometers were recorded. The maximum absorbance peak between these wavelengths was selected for each case and the absorbance values at this maximum for each solution were plotted against the concentration of dye in solution to obtain the calibration curve for the particular dye in the solution under consideration.

The commercial or impure forms of Acid Blue 25 and Acid Blue 145 were examined in solutions of distilled water and in solutions of methanol and water which contained 750 milliliters of methanol per liter of solution (75/25 methanol/water).

The absorbance-concentration relation was also examined for each of the impure acid dyes in distilled water solutions containing various

added chemicals in concentrations which were to be used in adsorption experiments. Dilutions of stock solutions of dyes containing added chemicals were made with solutions containing the proper amount of these added chemicals to insure that the concentrations of added chemicals remained constant as the concentration of dye varied. Calibrations were made for each of the acid dyes in aqueous solution containing a buffer of 0.5 g/l monohydrated sodium phosphate and 0.5 g/l disodium phosphate. Similarly, calibration curves were obtained for each of the acid dyes in aqueous solutions containing 0.5 g/l sulfuric acid, solutions with 1.0 g/l anhydrous sodium carbonate, and solutions with 5.0 g/l anhydrous sodium sulfate.

When samples of each of the acid dyes were purified, absorbance-concentration relations were plotted for their solutions in distilled water.

In all of the calibration experiments an attempt was made to perform dilutions of a stock solution of dye so that at least five different concentrations gave absorbance values in the range between zero and one. All solutions were examined at room temperature.

General Procedures

Standard procedures were developed for experiments involving the adsorption of dye from solution and the analysis of the final dye concentrations and amounts of dye adsorbed onto carbon. In each case 100 milliliters of dye solution of known concentration were placed in a 250 milliliter volumetric flask. One gram of granulated activated carbon was placed in the flask and the flask was stoppered. Flasks

were attached to the shaker and placed in the constant temperature bath. The elevation of flasks in the bath and the frequency of oscillation of the shaker were carefully controlled in all tests, so that all flasks received the same degree of agitation.

After predetermined times of contact, the flasks were removed from the bath and filtered using the Gelman filtering apparatus in order to remove carbon particles from solution. The filtered solutions were then diluted with the proper solvent to a point at which the solution could be examined on the spectrophotometer. The spectum of the diluted solution was recorded from 700 to 400 nm.

Before the absorbance at the wavelength of the maximum peak could be used with reference to the proper absorbance-concentration calibration curve to obtain the concentration of the diluted dye solution, a correction had to be made. The carbon was not completely removed by filtering, and thus, contributed to the absorbance values of dye solutions despite the multiple filtration procedure. The amount of error caused by the carbon varied depending on the solution and amount of dilution before analysis. A method was developed to correct the absorbance values for the contribution by carbon. The method involved the comparison of absorbance spectra of dye solutions treated with carbon to those of solutions which had not been in contact with carbon. The method is explained in Appendix B.

After the maximum absorbance values were corrected for carbon contribution, the proper absorbance-concentration calibration curve for the dye and solution under investigation was used to determine the concentration of the diluted solution. This concentration was multiplied

by the dilution factor to obtain the final dye concentration after contact with carbon. From this final concentration and the known original concentration and volume of solution, the amount of dye adsorbed per gram of carbon was easily calculated.

Rate Studies

Experiments which reflect the rate of adsorption of the dyes from solution onto carbon were conducted in order to determine a time of contact between carbon and dye solution which would result in conditions approximating those at equilibrium. In these rate studies 5.0 g/l solutions of the dye were treated with carbon according to the general procedure. The times of contact of solution with carbon were varied and in some cases the effect of temperature was examined.

Tests on impure Acid Blue 25 in distilled water, on impure Acid Blue 145 in distilled water, and on impure Disperse Blue 9 in 75/25 methanol/water included contact times of up to 252.3 hours at 25°C and up to 75 hours at 50°C. Tests on Disperse Blue 9 in distilled water included contact times of up to 75 hours at 25°C. After completion of the contact times, solutions were analyzed and the relation between the amount of dye adsorbed and time of contact was plotted.

The general procedure was slightly modified for Disperse Blue 9 in water. This dye is only slightly soluble in water at the temperatures used and is mainly held in suspension by a dispersing agent present in the commercial dye. In order to avoid loss of dye on the filter paper during filtration, the dye in water was diluted with methanol and 75/25 methanol/water before filtration.

The results of these rate studies were instrumental in determining reasonable times of contact between dye solutions and carbon, so that conditions approximating equilibrium could be established.

Establishment of Isotherms

After contact times yielding approximate equilibrium conditions were established, the effects of varying dye molecular structure, temperature, pH, salt content, surfactant content, and solvent were studied. Approximate equilibrium isotherms were obtained under varying conditions and these isotherms were compared in order to make judgments on the effects of certain factors on dye adsorption.

The general procedures governing the handling of dye solutions in contact with carbon and the analysis of solutions after carbon contact were followed.

Variations in Dye Molecular Structure

The effects of variation in dye structure on adsorption were examined by determining and comparing adsorption isotherms for the three dyes.

Stock solutions of all three dyes in distilled water were prepared containing 5.0 g/l of impure dye. Solutions of Acid Blue 25 were prepared from the stock solution which encompassed six different initial concentrations (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l), and these samples were contacted with carbon for 50 hours at 25°C. Solutions of Acid Blue 145 and of Disperse Blue 9, each with six different initial concentrations ranging from 5.0 to 2.0 g/l, were run for 50 hours at 25°C. The same modification of the general procedure was used with Disperse

Blue 9 in water as in the rate study.

Although the main concern of this work is adsorption from water, it was thought that examination of the dyes in 75/25 methanol/water might yield information on specific effects of dye structure on adsorption. Stock solutions of all three dyes containing 5.0 g/l of impure dye were prepared in 75/25 methanol/water. Solutions of Acid Blue 25 were prepared containing eight different concentrations of dye (5.0, 4.5, 4.0, 3.5, 3.0, 2.7, 2.5, and 2.4 g/l), and they were run from 50 hours with carbon at 25°C. Six solutions of Acid Blue 145 were prepared (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l), and run for 50 hours at 25°C. Six Disperse Blue 9 solutions in alcohol/water (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l) were run for 25 hours at 25°C.

When purified samples of Acid Blue 25 and Acid Blue 145 had been secured, stock solutions in distilled water were made. Three concentrations of Acid Blue 25 (2.50, 1.63, and 1.25 g/l) were run with carbon for 50 hours at 25°C. Purified Acid Blue 145 solutions (1.8, 1.6, and 1.5 g/l) were also run for 50 hours at 25°C.

Temperature Effects

Distilled water solutions of impure Acid Blue 25 and impure Acid Blue 145 were contacted with carbon for 50 hours at 50°C, and 75/25 methanol/water solutions of impure Disperse Blue 9 were contacted with carbon for 25 hours at 50°C in order to examine the effects of elevated temperature on adsorption. Eight samples of Acid Blue 25 were examined (5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, and 1.5 g/l). Seven samples of Acid Blue 145 were run (5.0, 4.5, 4.0, 3.5, 3.0, 2.5, and 2.0 g/l). Six samples of Disperse Blue 9 were studied (5,0, 4.5, 4.0, 3.5, 3.0,

and 2.5 g/l).

Results from these tests were compared to those from tests at 25°C.

pH Effects

The effects of pH variation on adsorption were studied using the impure forms of Acid Blue 25 and Acid Blue 145 in distilled water. Three different pH levels (acidic, nearly neutral, and basic) were chosen for each dye. In every pH effect test the contact time was 50 hours and the temperature was 25°C. Measurements of the pH of these solutions were made.

A low pH was obtained by incorporating 0.5 g/l of sulfuric acid into the 5.0 g/l stock solutions of the dyes in water. A 0.5 g/l aqueous solution of sulfuric acid was used in all dilutions of the dye solutions and as a reference when the solutions were analyzed spectrophotometrically. Six dye concentrations were run for each dye (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l).

A pH near seven was achieved by adding 0.5 g/l monohydrated sodium phosphate and 0.5 g/l anhydrous disodium phosphate to the 5.0 g/l stock solutions of the dyes. All dilutions were made with an aqueous solution containing 0.5 g/l of each of the buffer components. This solution was also used in the reference cell. Again, six concentrations of each of the dyes were examined (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l).

A high pH was maintained by adding 1.0 g/l of anhydrous sodium carbonate to the 5.0 g/l stock dye solutions. A solution of 1.0 g/l sodium carbonate in water was used in all dilutions and in the reference cell of the spectrophotometer. Six concentrations of each dye were con-

tacted with carbon (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l).

Electrolyte Effect

The effect of a large concentration of inorganic electrolyte on the adsorption of both acid dyes was examined.

Stock solutions of impure Acid Blue 25 and impure Acid Blue 145 were prepared in distilled water which included 5.0 g/l anhydrous sodium sulfate. A 5.0 g/l solution of the salt was used in all dilutions and in the reference cell of the spectrophotometer. Six different concentrations of each dye (5.0, 4.5, 4.0, 3.5, 3.0, and 2.5 g/l were contacted with carbon for 50 hours at 25°C.

Surfactant Effect

The effect of the presence of Igepon T in water solution with impure Acid Blue 145 on the adsorption of the dye was determined. Two sets of dye solutions in water, each containing a sample with 5.0, 4.0, and 2.5 g/l of dye, were run with surfactant and carbon. In the first set each solution contained 1.0 g/l of the active ingredient of Igepon T. In the second set 2.0 g/l of the active ingredient were included. Samples were run with carbon for 50 hours at 25°C.

The reference cell of the spectrophotometer was filled with distilled water during the analysis of these solutions after contact with carbon.

A 100 g/l solution of the Igepon T in water was analyzed spectrophotometrically in order to help assess the contribution of the surfactant to the absorbance values of the dye solution. Its spectrum from 700 to 400 nm was established.

Solvent Effect

The effect of differing solvents on the adsorption of dye by carbon was studied by comparing the isotherms of the dyes in distilled water with those in 75/25 methanol/water.

Determination of Purities of Dyes

In order to compare the adsorption of the different dyes on a molar basis and make any conclusions about the effects of dye molecular structure on adsorption, the purities of the dyes had to be determined. When pure samples of Acid Blue 25 and Acid Blue 145 were obtained according to the procedures in Appendix C, absorbance-concentration calibration curves were obtained and compared to the calibration curves of the impure dyes in order to arrive at the purity of the dyes.

CHAPTER IV

DISCUSSION OF THE RESULTS

Calibration Curves

The experiments on the absorbance-concentration relationship for the dyes in various solutions yielded curves which showed a linear dependence of absorbance on concentration, in agreement with Beer's Law. The calibration curves for pure and impure Acid Blue 25 and pure and impure Acid Blue 145 are found in Figure 2. Calibration tests run with the two impure acid dyes in water solution in the presence of the various added chemicals described in the previous chapter showed that linear relations held for all solutions and that calibration curves of solutions with added chemicals matched well the curves of the impure dyes in water without added chemicals.

Calibration curves of the three impure dyes in 75/25 methanol/water are shown in Figure 3. The two acid dyes show excellent linear relations between absorbance and concentration. The impure Disperse Blue 9 calibration data gives a reasonable approximation to a linear relation between absorbance and concentration.

The wavelengths of the absorbance maxima and the calculated specific absorbances (1.0 g/l) are given in Table 1.

Determination of Dye Purities

After samples of purified Acid Blue 25 and Acid Blue 145 were obtained and the absorbance-concentration calibrations of these pure dyes

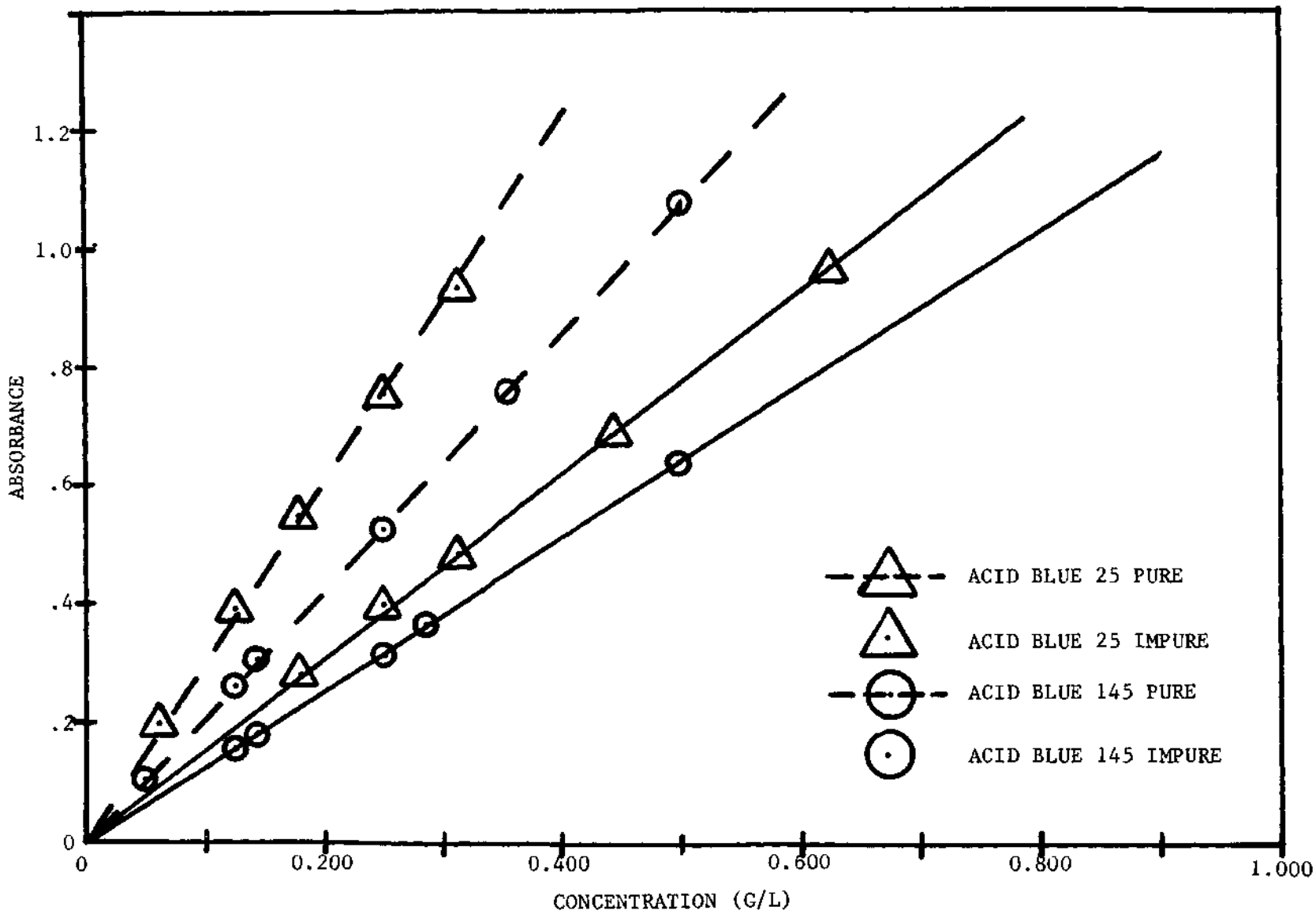


Figure 2. Absorbance-Concentration Relations for Pure and Impure Acid Dyes in Water

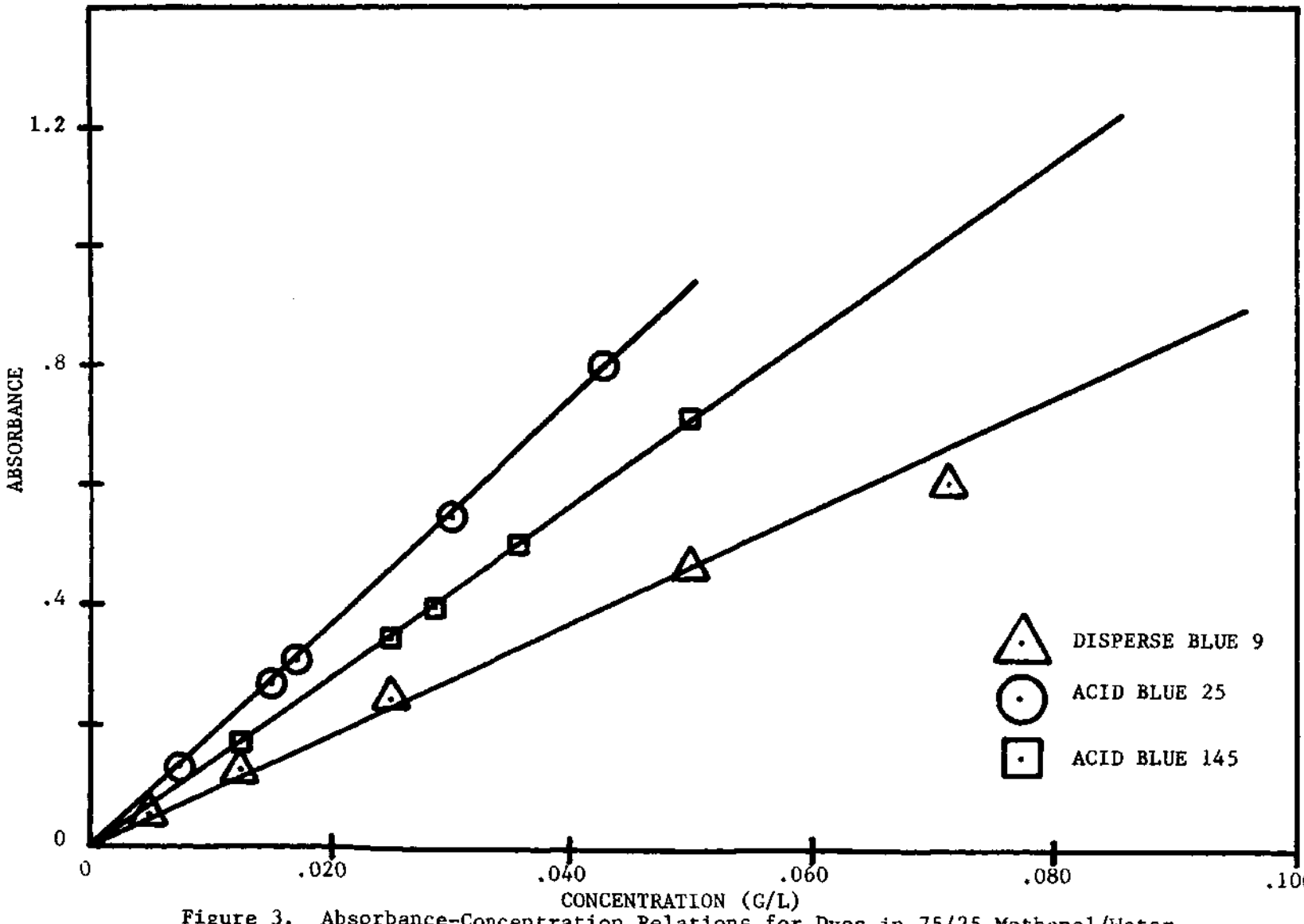


Figure 3. Absorbance-Concentration Relations for Dyes in 75/25 Methanol/Water

Table 1. Wavelengths of Absorbance Maxima and Specific Absorbances for Dye Solutions

Name of Dye	Medium	Added Chemicals	Wavelength of Maximum (nm)	Specific Absorbance*
Impure Acid Blue 25	Water	None	600	15.4
Impure Acid Blue 25	Water	0.5 g/l H_2SO_4	600	15.6
Impure Acid Blue 25	Water	Phosphate Buffer	600	15.6
Impure Acid Blue 25	Water	1.0 g/l Na_2CO_3	600	15.6
Impure Acid Blue 25	Water	5.0 g/l Na_2SO_4	600	15.2
Impure Acid Blue 25	75/25 Methanol/Water	None	627	18.3
Pure Acid Blue 25	Water	None	600	30.0
Impure Acid Blue 145	Water	None	602	12.7
Impure Acid Blue 145	Water	0.5 g/l H_2SO_4	602	12.5
Impure Acid Blue 145	Water	Phosphate Buffer	602	12.8
Impure Acid Blue 145	Water	1.0 g/l Na_2CO_3	602	12.5
Impure Acid Blue 145	Water	5.0 g/l Na_2SO_4	602	12.6
Impure Acid Blue 145	75/25 Methanol/Water	None	600	14.2
Pure Acid Blue 145	Water	None	602	21.1
Impure Disperse Blue 9	75/25 Methanol/Water	None	620	9.4

*1.0 g/l, 1 cm silica cell

in distilled water were completed, it was a simple matter to compare calibration curves for pure and impure dyes and determine the degree of purity of the commercial dyes. The ratio of the concentration (g/l) of the pure dye to that of the commercial dye at any given absorbance value would yield the purity. The Acid Blue 25 was found to be 53 percent pure and the Acid Blue 145 was found to be 58 percent pure.

Attempts to purify Disperse Blue 9 were not successful. The difficulty was thought to arise from the presence of a dispersing agent in the commercial dye which was very difficult to separate from the dye itself. Both of the attempted methods of purification outlined in Appendix B apparently failed because when attempts were made to dissolve the product of the procedures in 75/25 methanol/water, portions of this product were found to be insoluble even in hot solvent. Methanol/water is known to be a good solvent for disperse dyes, and so, there must have been something other than disperse dye in the products of the purification procedures. Perhaps this insoluble matter was the dispersing agent which may have been modified in the purification treatments.

An estimate of the purity of Disperse Blue 9 was made in a manner which did not involve actual purification of the dye. It was assumed that since the three dyes were of such similar molecular structures, their molar extinction coefficients would be of similar magnitude. Keeping this assumption in mind and knowing the purities of the acid dyes, an estimate of the purity of the disperse dye was made using the calibration curves of all three dyes in 75/25 methanol/water and the molecular weights of the dyes. Molar extinction coefficients for both acid dyes in 75/25 methanol/water were calculated from points on the

calibration curves of the dyes in alcohol/water, using molecular weights and known purities of the dyes. The calculated molar extinction coefficients in 75/25 methanol/water for Acid Blue 25 and Acid Blue 145 were found to be 14.6×10^3 and 13.1×10^3 absorbance units per mole per liter respectively. The average of these was used as the extinction coefficient for Disperse Blue 9. A point on the calibration curve of Disperse Blue 9 in alcohol/water was chosen and the absorbance and concentration at this point along with the calculated molar extinction coefficient and molecular weight of Disperse Blue 9 were used to calculate the approximate purity of the dye from the following equation.

$$\frac{A_p \cdot M}{C_p \cdot X} = E_m$$

A_p is the absorbance at the chosen point and C_p is the corresponding concentration. M is the molecular weight, E_m the extinction coefficient, and X is the purity. The result was a calculated approximate purity of 23 percent.

Rate Studies

The amounts of impure Acid Blue 25 adsorbed from water for various times of contact with carbon are plotted in Figure 4 for experiments at 25°C and 50°C. Curves at both temperatures show a rapid initial increase in amounts adsorbed with time. After 25 hours the curves begin to level off, but at least in the case of the 25°C experiment, adsorption continues slowly after even 75 hours. The fifty hour points on both curves are past the initial steep portions of the curves and on the gradually increasing portions. Fifty hours was chosen as the

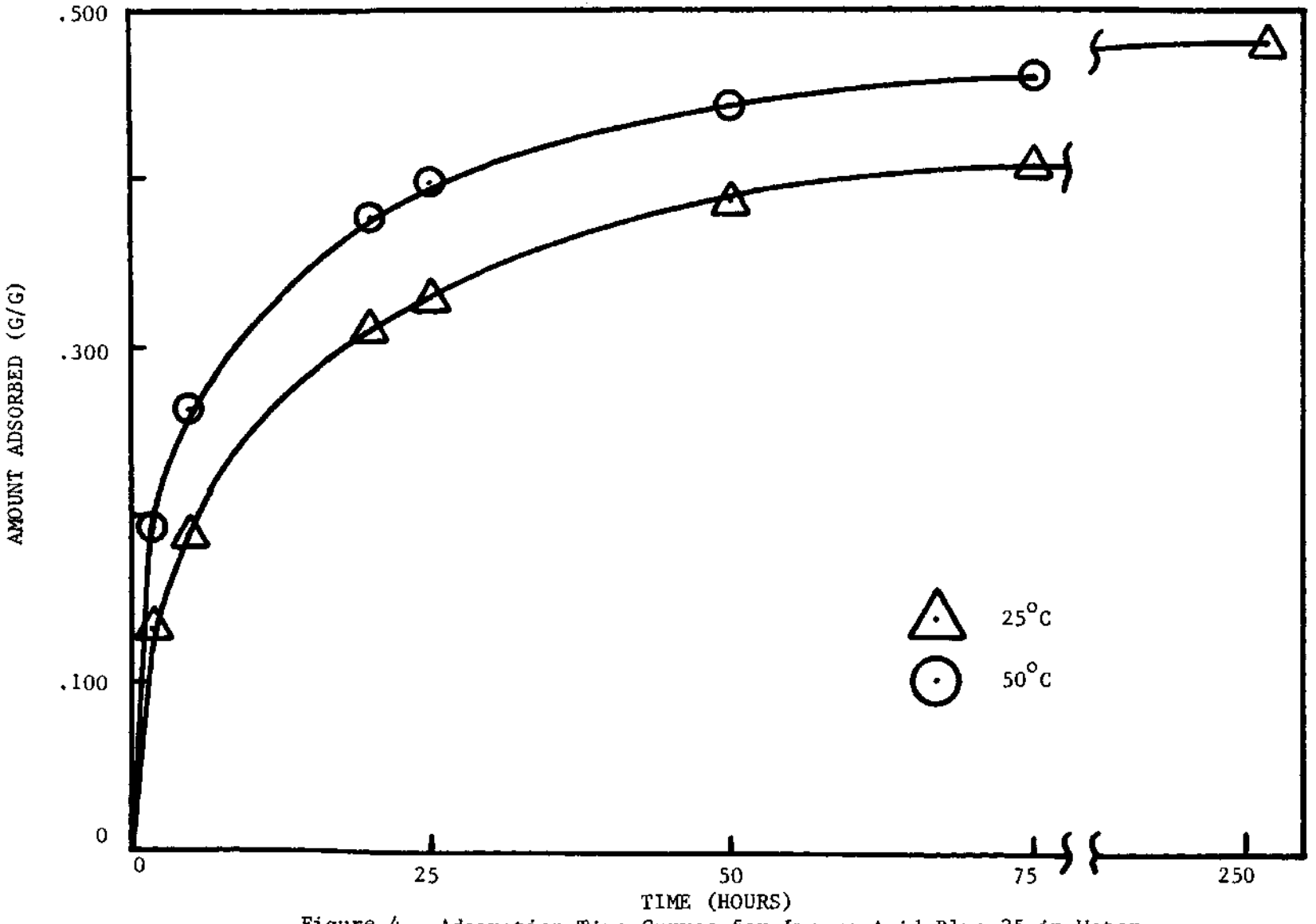


Figure 4. Adsorption-Time Curves for Impure Acid Blue 25 in Water

contact time for solutions of Acid Blue 25 in water. Although the system is not truly at equilibrium, the rate of adsorption after 50 hours is so slow that conditions at 50 hours may be fairly good indications of conditions at true equilibrium. This fifty hour contact time was applied to all solutions containing Acid Blue 25; however, it must be remembered that 50 hours does not represent the time to achieve equilibrium, and that rate effects must be considered in comparing adsorption isotherms of Acid Blue 25 from different types of solutions.

The higher adsorptions at the higher temperature probably indicate an increased rate of adsorption at the higher temperature, since the difference between the elevations of the two curves at particular times generally decreases slowly with time. Figure 40 (Appendix D) shows reciprocal adsorption-time plots which converge to approximately the same point, indicating that the increased temperature changes the rate of adsorption but does not greatly alter the equilibrium state.

Figure 5 shows the adsorption of impure Acid Blue 145 from water at various times at temperatures of 25°C and 50°C. The curve shapes are similar to those for Acid Blue 25. The rapid initial adsorption is followed by a gradual increase in adsorption after 25 hours. The adsorbed amounts are greater at all times at the higher temperature but the magnitude of difference generally decreases with time. This probably reflects a higher rate of adsorption at the higher temperature. The reciprocal plots in Figure 41 (Appendix D) converge to approximately the same intercept, and indicate that the temperature change does not appreciably alter equilibrium conditions.

Fifty hours was chosen as the contact time to achieve an approx-

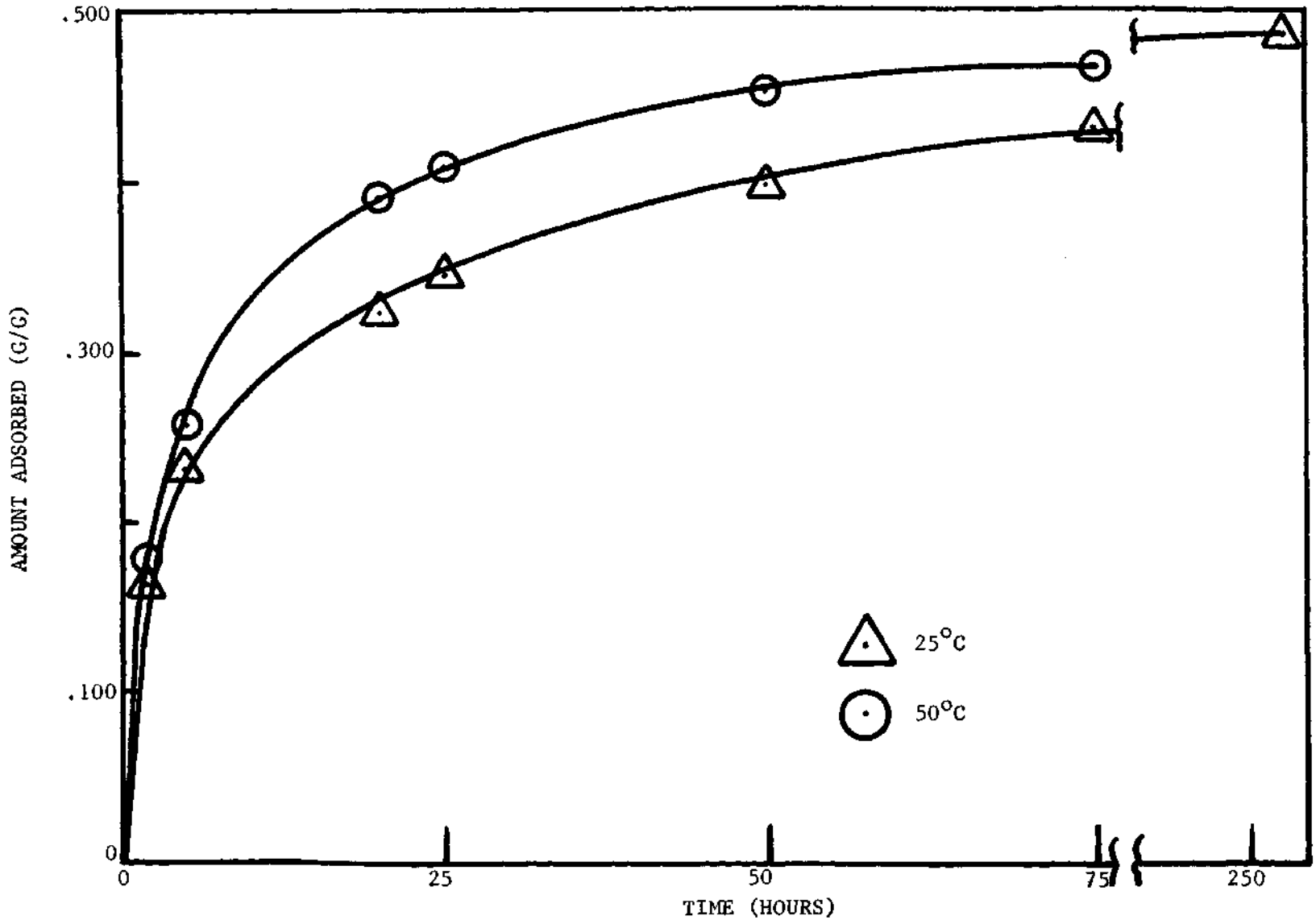


Figure 5. Adsorption-Time Curves for Impure Acid Blue 145 in Water

imation to equilibrium conditions for Acid Blue 145 solutions due to the position of the fifty hours adsorption point on the gradually increasing portion of the curve.

Figure 6 shows the results obtained for the adsorption of Disperse Blue 9 from water at 25°C at various times. It appears that adsorption occurred rapidly under 20 hours and then leveled off after 20 hours to a gradual increase with time. Fifty hours was chosen as an acceptable contact time to achieve conditions approximate to equilibrium. The Disperse Blue 9 in water formed a dispersion rather than a true solution of the dye, and the problem of precipitation of the dye from the liquid may have been a source of error in the results obtained. The Disperse Blue 9 was adsorbed to a much lesser extent than the acid dyes.

Figure 7 includes an adsorption-time curve for impure Disperse Blue 9 in 75/25 methanol/water at 25°C and one at 50°C. The major share of the adsorption takes place very quickly and the curves level off to an extremely gradual increase in adsorption with time at about ten hours. Twenty-five hours was chosen as the contact time with carbon for solutions of Disperse Blue 9 in 75/25 methanol/water.

The higher temperature has the effect of increasing the amount of adsorption of Disperse Blue 9 at a particular time after the first five hours passed. The magnitude of the difference between adsorbed amounts at a particular time for curves at the two temperatures was seen to increase slightly with time, indicating possible higher equilibrium adsorption of the dye at the higher temperature. Figure 43 (Appendix D) shows reciprocal adsorption-time plots at the two temper-

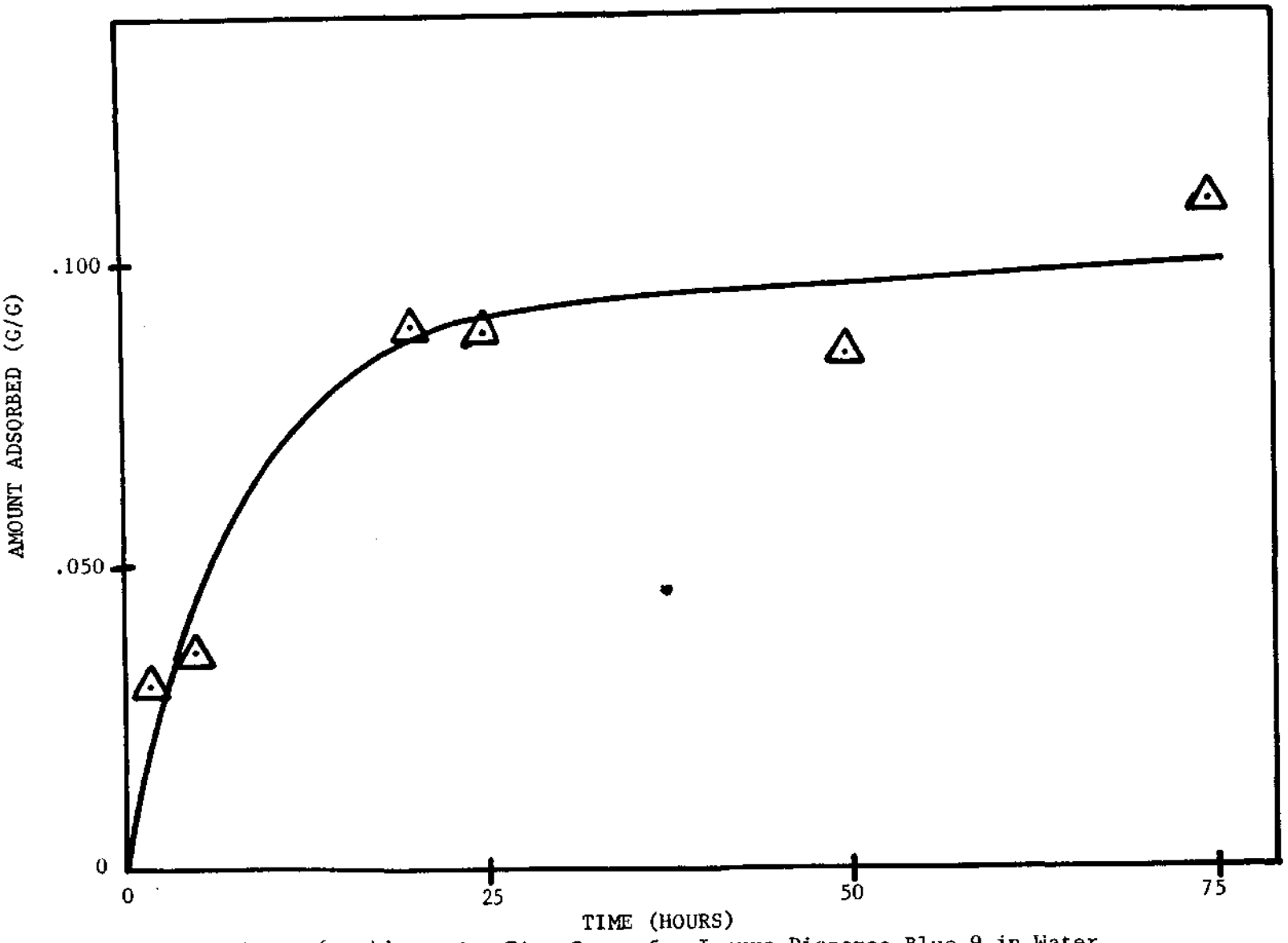


Figure 6. Adsorption-Time Curve for Impure Disperse Blue 9 in Water

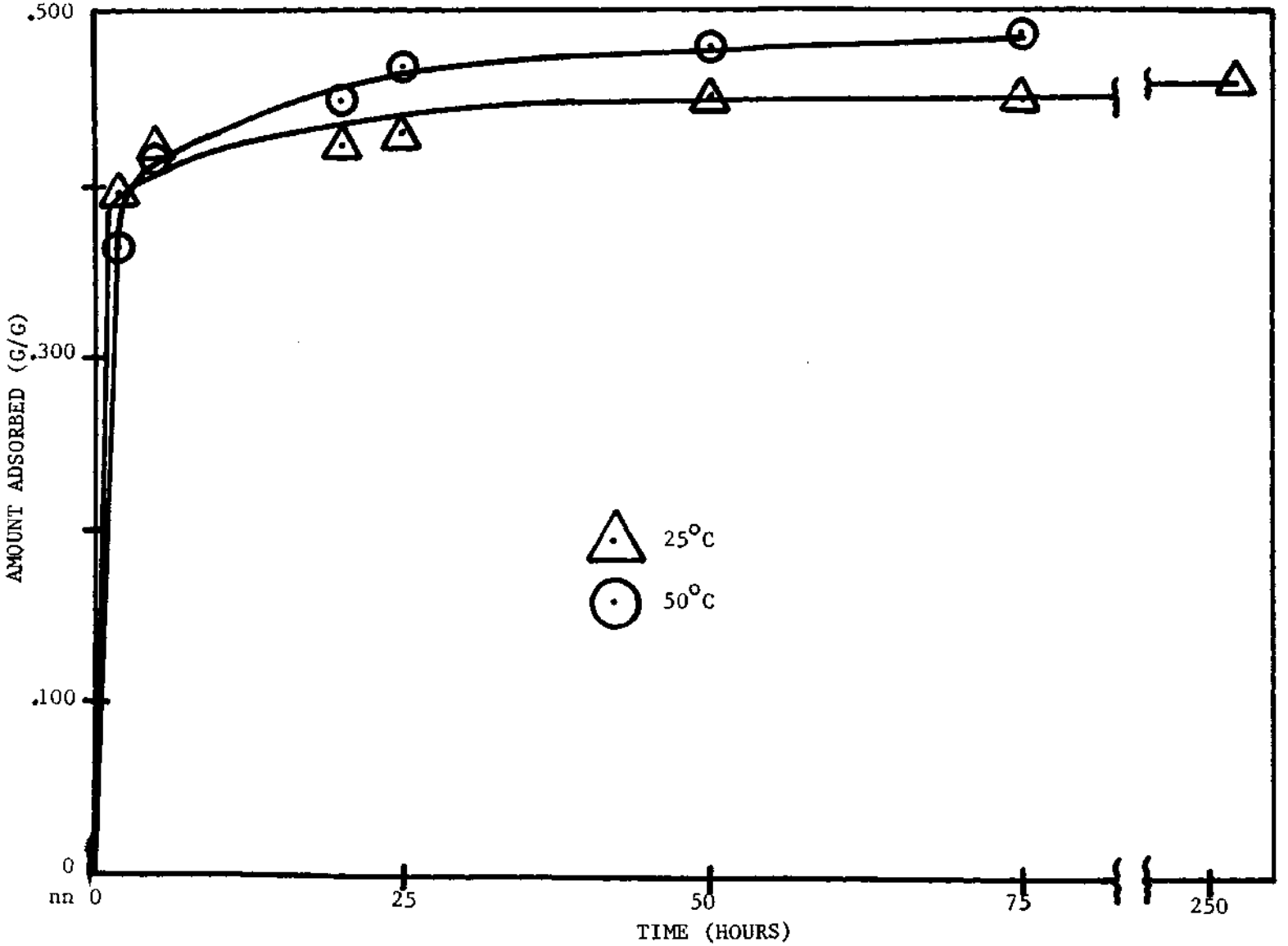


Figure 7. Adsorption-Time Curves for Impure Disperse Blue 9 in 75/25 Methanol/water

atures which are nearly parallel with different intercepts, indicating a higher equilibrium adsorption at the higher temperature.

The adsorption of Disperse Blue 9 from methanol/water was much greater than that from water.

The contact times chosen for all Acid Blue 25 solutions, all Acid Blue 145 solutions, the Disperse Blue 9 in water, and the Disperse Blue 9 in alcohol/water are not times which yield actual equilibrium conditions, but from the shapes of the adsorption time curves, it was felt that the selected times would yield conditions reflecting those at equilibrium. The equilibrium adsorptions for all four systems were estimated from reciprocal plots of adsorption versus time (Appendix D). Comparisons of estimated equilibrium adsorptions to the adsorptions at the selected contact times are given in Table 2.

Isotherms

All data on isotherms is presented graphically in the text. Both arithmetic and full logarithmic plots of the amount of dye adsorbed per gram of carbon versus the final concentration of dye in solution are given.

Variation in Dye Molecular Structure

Figure 8 shows adsorption isotherms for all three dyes in distilled water at 25°C. Results are expressed as molar quantities (millimoles) obtained by taking the dye purities into consideration. Figure 9 is a full logarithmic plot of the data.

The adsorption of impure Acid Blue 25 and Acid Blue 145 appear to be almost the same with possibly slightly greater adsorption of the Acid Blue 25 at higher concentration of dye in solution. The adsorp-

Table 2. Comparison of Estimated Equilibrium Adsorptions to Adsorptions at Selected Contact Times

Dye	Solvent	Temperature (^{o}C)	Value of Amount Adsorbed (G/G) where 1/Time = 0	Selected Contact Time (hours)	Amount Adsorbed (G/G) at Selected Contact Time	Percentage of Equilibrium Adsorption at Selected Contact Time
Impure Acid Blue 25	H_2O	25	.493	50	.387	79
Impure Acid Blue 25	H_2O	50	.494	50	.443	90
Impure Acid Blue 145	H_2O	25	.490	50	.398	81
Impure Acid Blue 145	H_2O	50	.495	50	.452	91
Impure Disperse Blue 9	H_2O	25	.129	50	.085	66
Impure Disperse Blue 9	75/25 Methanol/Water	25	.465	25	.430	93
Impure Disperse Blue 9	75/25 Methanol/Water	50	.498	25	.468	94

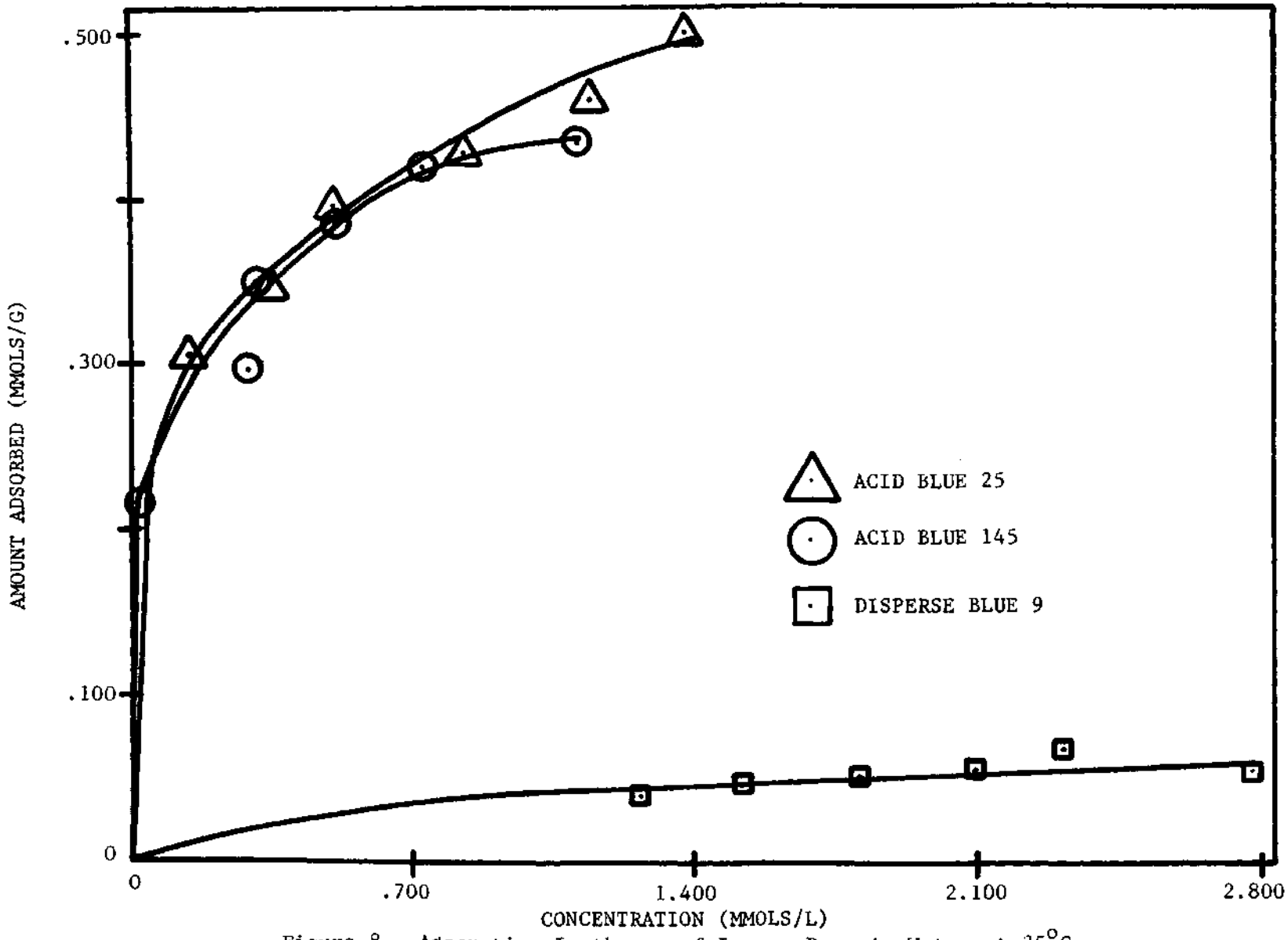


Figure 8. Adsorption Isotherms of Impure Dyes in Water at 25°C

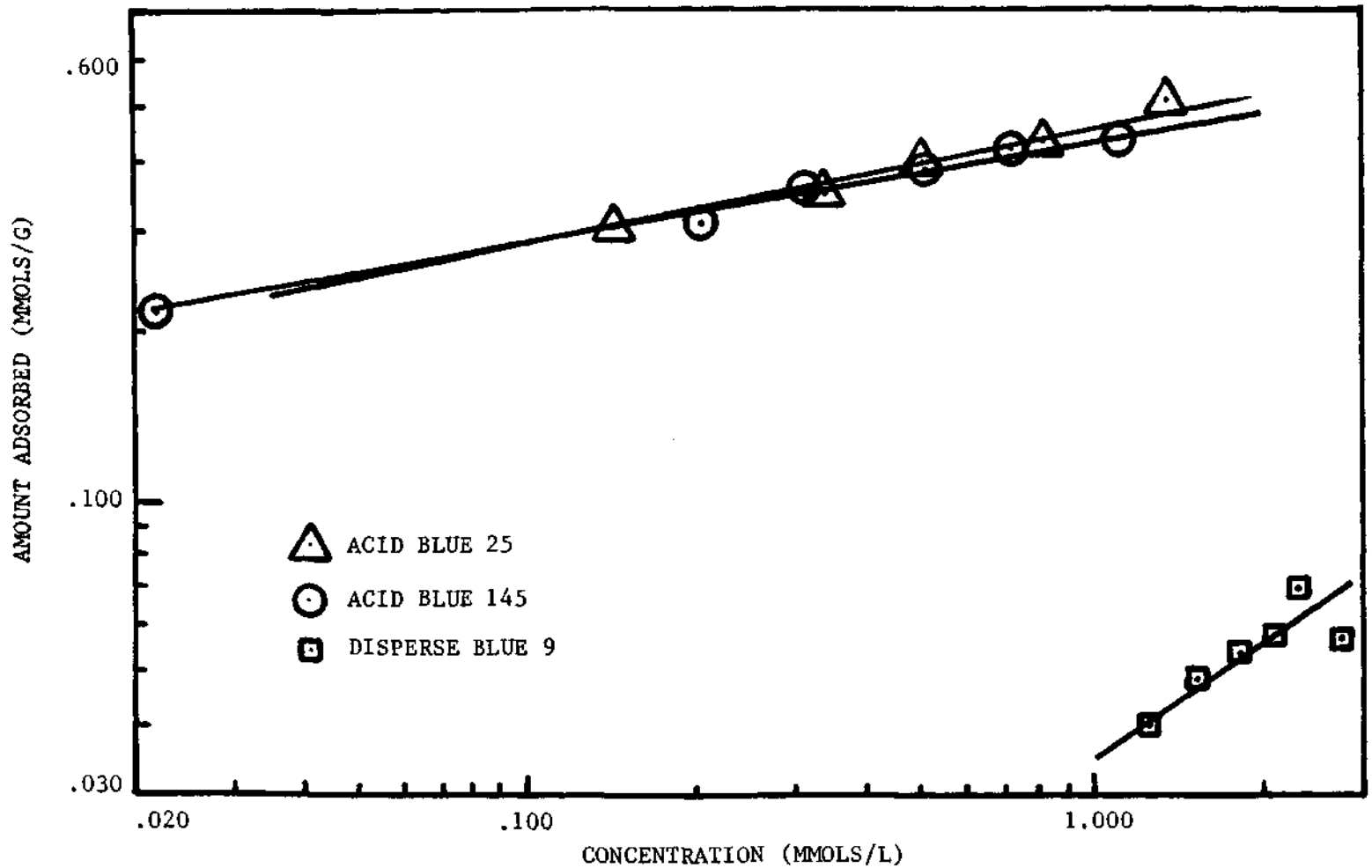


Figure 9. Adsorption Isotherms of Impure Dyes in Water at 25°C

tion of impure Disperse Blue 9 is seen to be considerably lower than that of either acid dye.

A possible explanation of the low adsorption of disperse dye is that the dye is not truly in solution. Aggregates of dye molecules are suspended in the water by a dispersing agent present in the commercial dye. The pore sizes in the carbon prevent extensive adsorption of these aggregates and possibly only the small amounts of dye molecules which actually go into water solution are adsorbed along with some of the smaller dye aggregates. The lack of dye solubility in water and the presence of the dispersing agent hamper the evaluation of the adsorption of the disperse dye molecules from water.

The impurities present in the acid dyes have an effect on the adsorption of the dye molecules from water. Figures 10, 11, 12, and 13 illustrate the effects of these impurities. Pure Acid Blue 25 was adsorbed to a greater extent than the impure dye, particularly at the lesser concentrations of dye. Pure Acid Blue 145 appears to be adsorbed to a greater extent at low concentrations and to a lesser extent at higher concentrations in solution than impure Acid Blue 145.

The presence of impurities in the commercial dyes hamper the evaluation of the effect of dye structure on adsorption of the dyes from water. After consideration of the effects of the impurities evidenced in Figures 10, 11, 12, and 13, it might be conjectured that the monosulfonated Acid Blue 25 would be adsorbed to a greater extent than the disulfonated Acid Blue 145, if the effects of the dye impurities were removed.

Figures 14 and 15 compare the isotherms of Acid Blue 25 and Acid

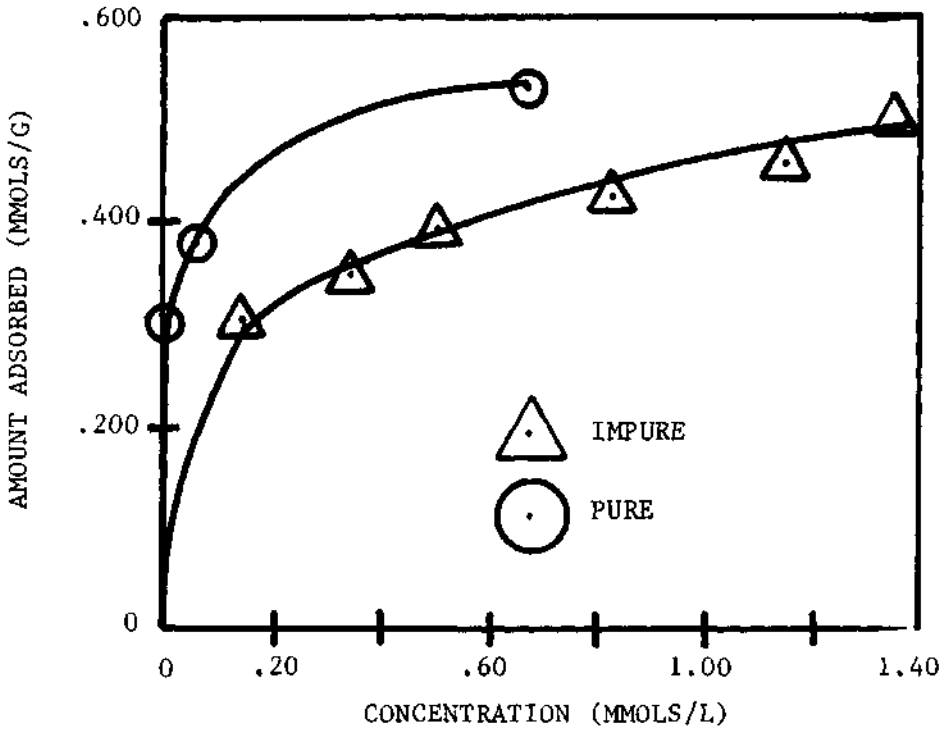


Figure 10. Isotherms for Pure and Impure Acid Blue 25 in Water at 25°C

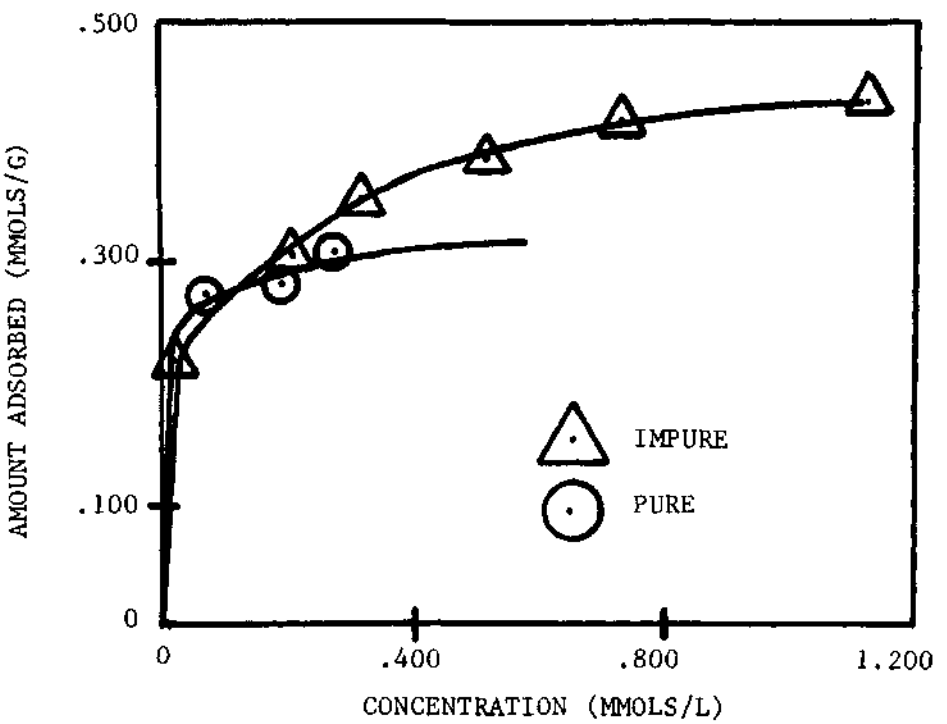


Figure 11. Isotherms for Pure and Impure Acid Blue 145 in Water at 25°C

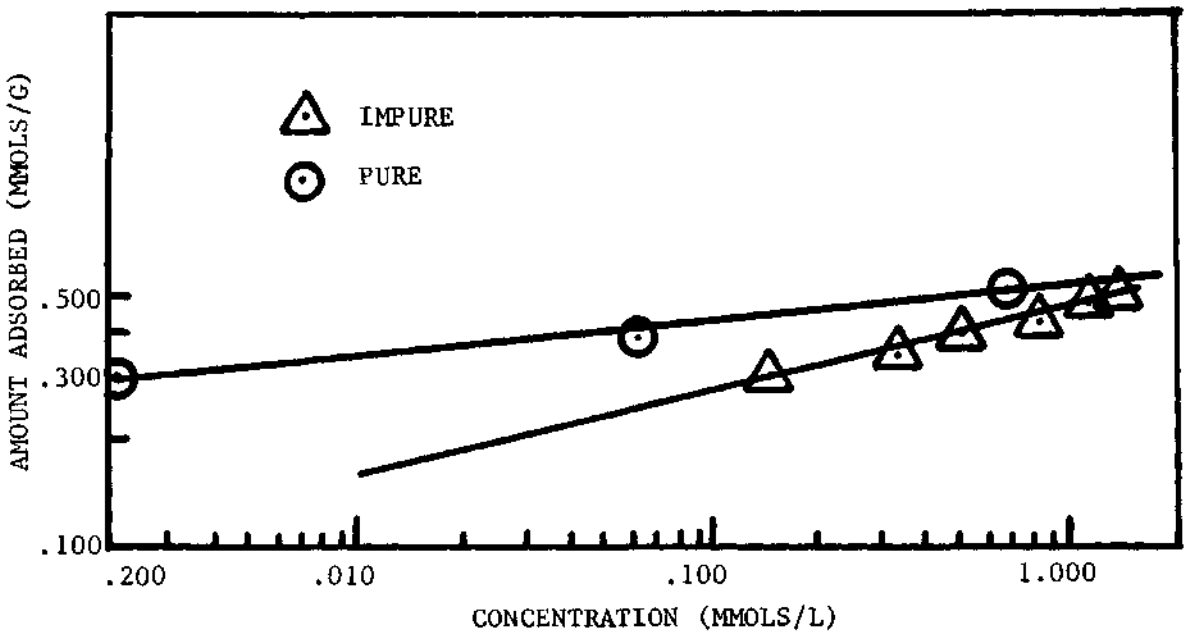


Figure 12. Isotherms for Pure and Impure Acid Blue 25 in Water at 25°C

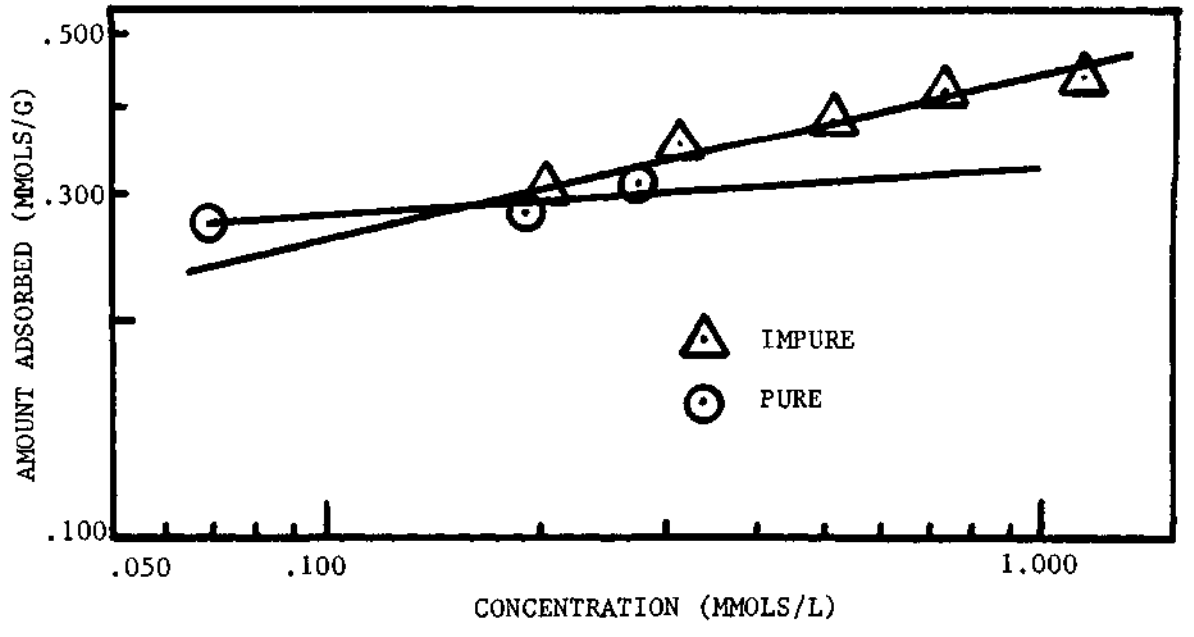


Figure 13. Isotherms for Pure and Impure Acid Blue 145 in Water at 25°C

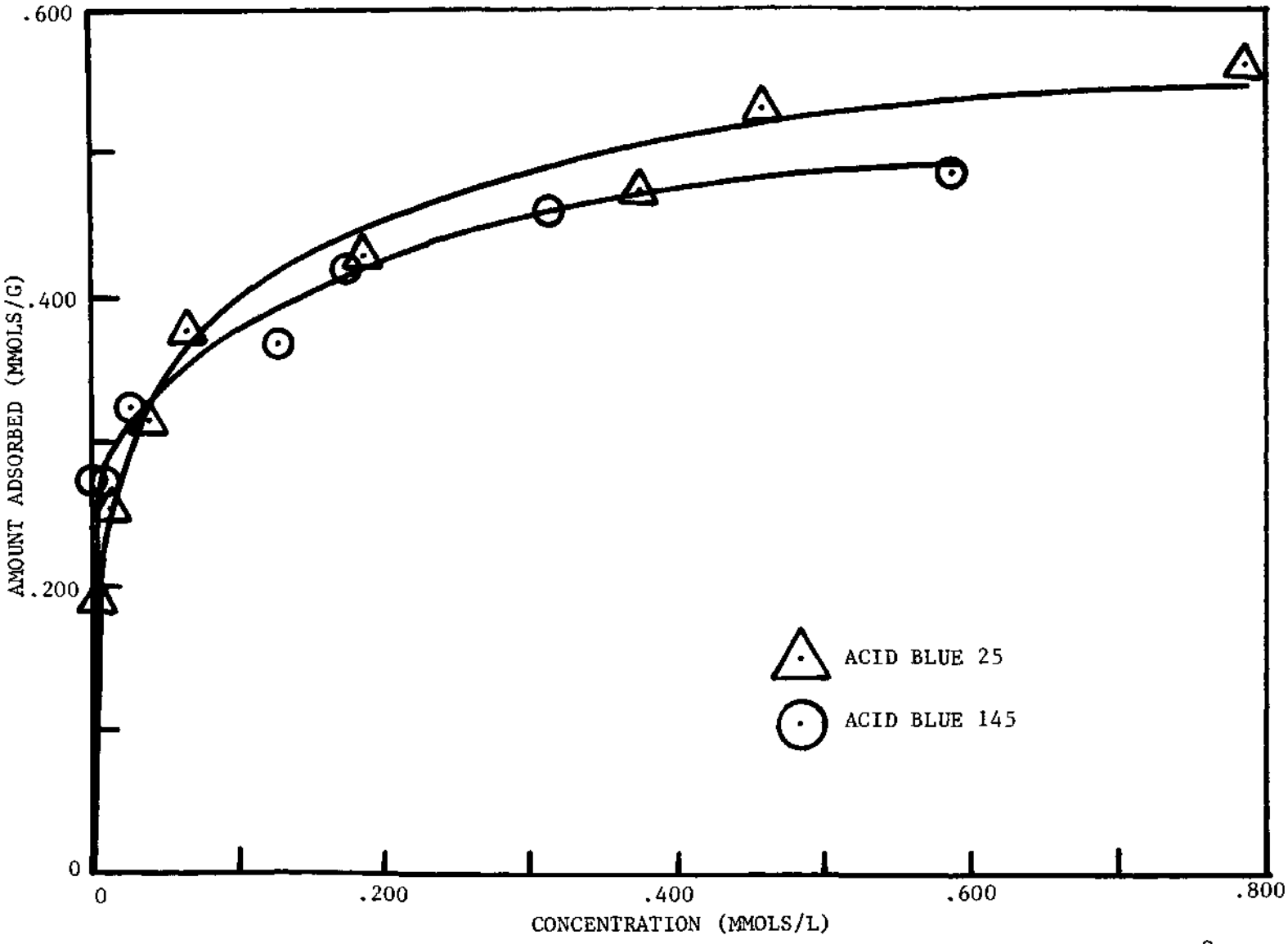


Figure 14. Isotherms for Impure Acid Blue 25 and Impure Acid Blue 145 in Water at 50°C

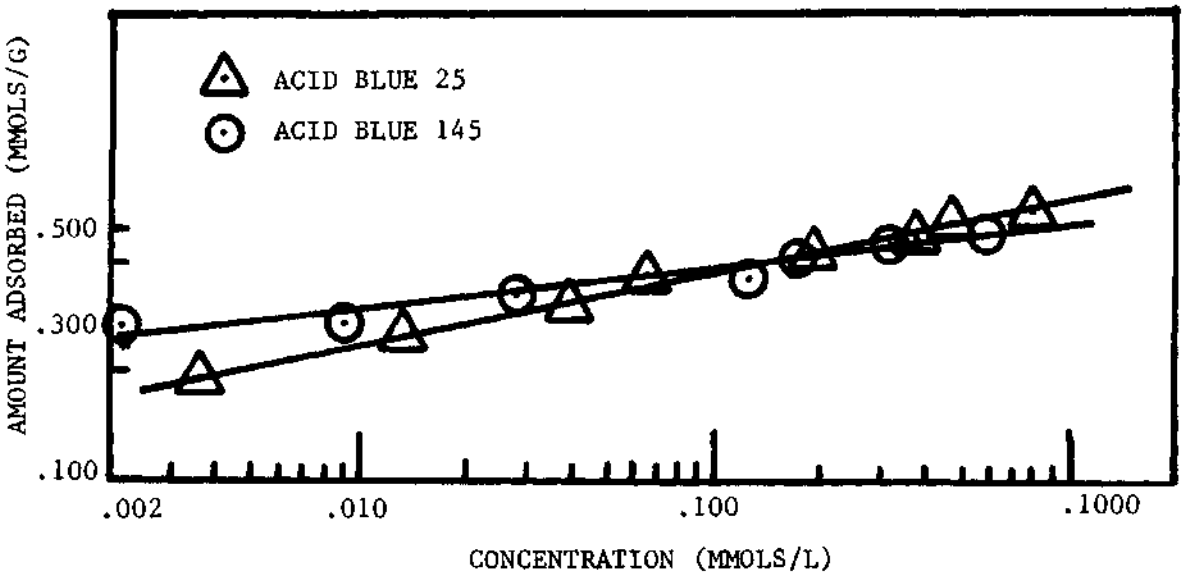


Figure 15. Isotherms for Impure Acid Blue 25 and Impure Acid Blue 145 in Water at 50°C

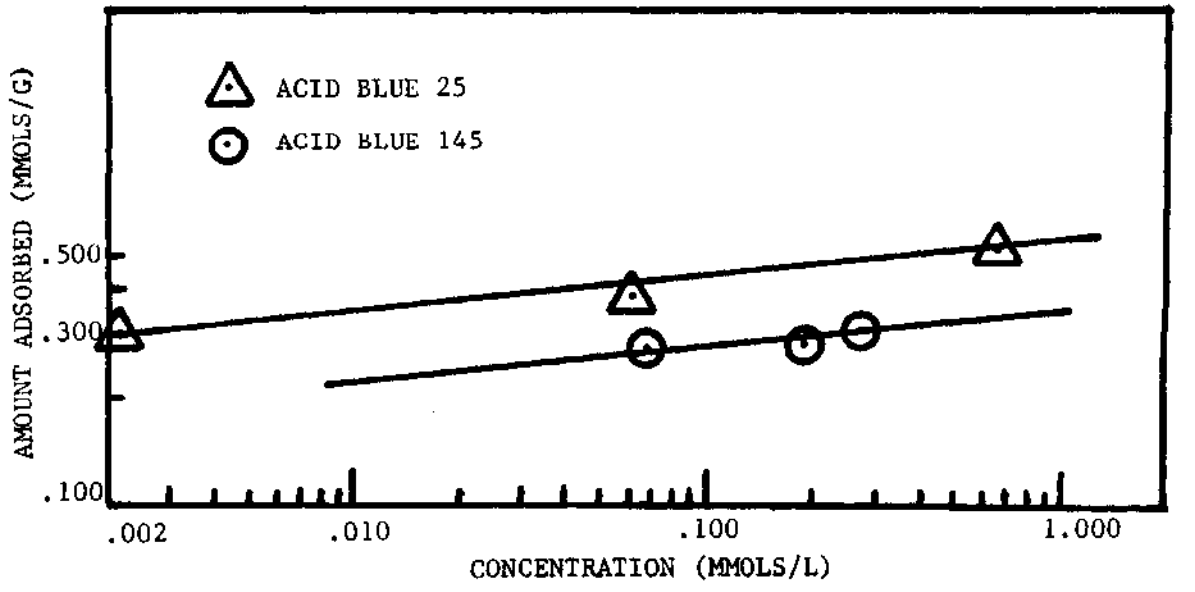


Figure 16. Isotherms for Pure Acid Blue 25 and 145 in Water at 25°C

Blue 145 in water at 50°C. The results are similar to those at 25°C. The dyes are adsorbed in similar amounts with the Acid Blue 145 adsorbed to a slightly lesser extent than the Acid Blue 25 at the higher concentrations and to a slightly greater extent at the lower concentrations. Again, the effects of impurities cloud the interpretation of results but it might be surmised that the monosulfonated Acid Blue 25 would be adsorbed more than the disulfonated Acid Blue 145, if impurity effects were removed, since the results with impurity effects show such similar degrees of adsorption.

Isotherms established from three points for pure Acid Blue 25 and pure Acid Blue 145 solutions in water at 25°C were compared in Figures 16 and 17. These isotherms give the best evidence for the effect of dye structure on adsorption. The additional sulfonic acid group on the Acid Blue 145 apparently causes the adsorption of the disulfonated dye to be less than that of monosulfonated Acid Blue 25. The effect of the additional sulfonic acid group, as explained by Hassler (17), may be attributed to possible increased solubility in water which the additional ionizable group might confer on Acid Blue 145. The effect of the additional methyl group on Acid Blue 145 is not thought to contribute much to the difference in adsorption, since it is much less chemically active than the sulfonic acid group.

Figures 18 and 19 are comparisons of the adsorption isotherms of all three impure dyes from 75/25 methanol/water at 25°C. Acid Blue 25 was adsorbed to the greatest extent with the difference between its adsorption and that of the other two dyes decreasing with increased concentration of solution. In the concentration range studied it appeared

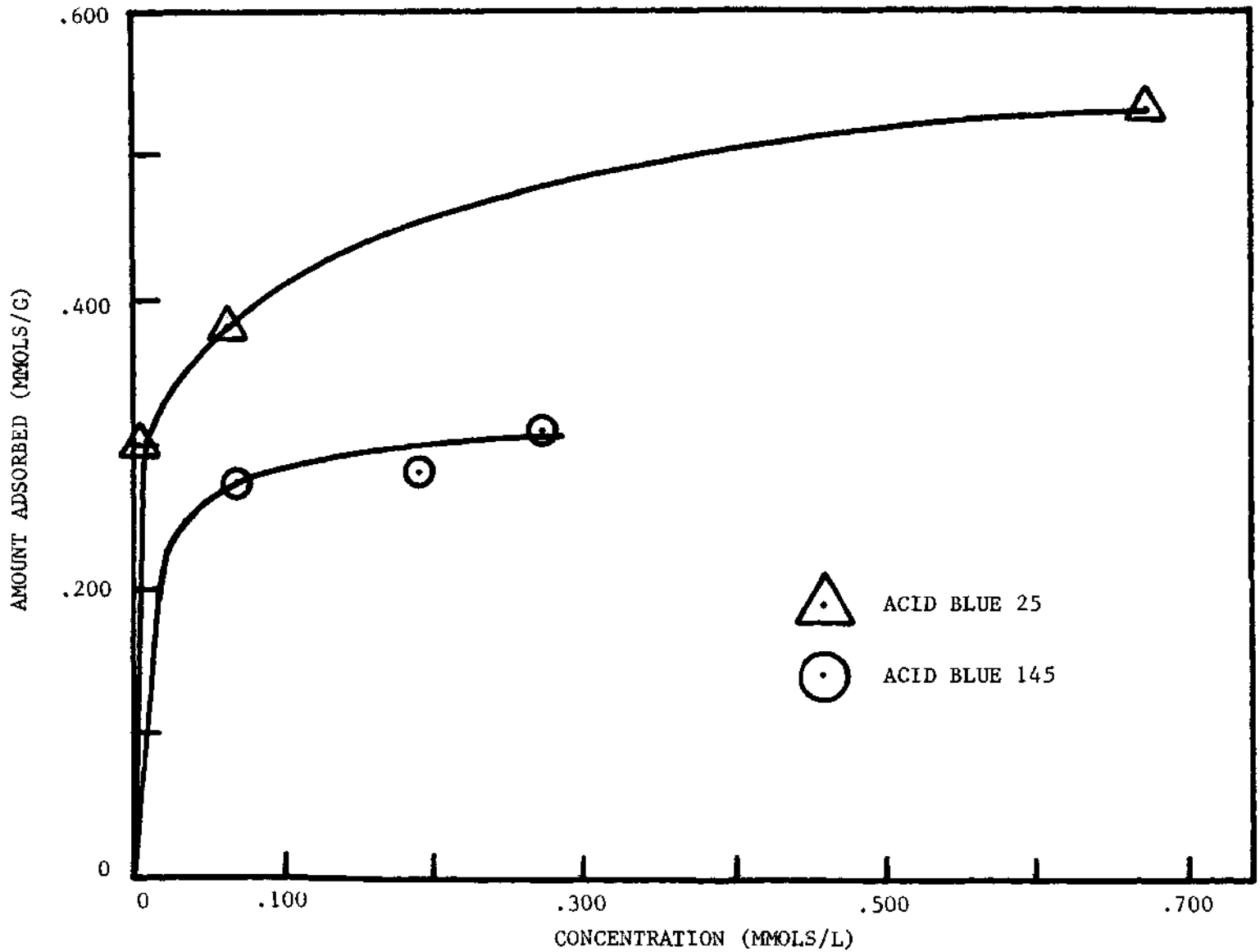


Figure 17. Isotherms for Pure Acid Blue 25 and 145 in Water at 25°C

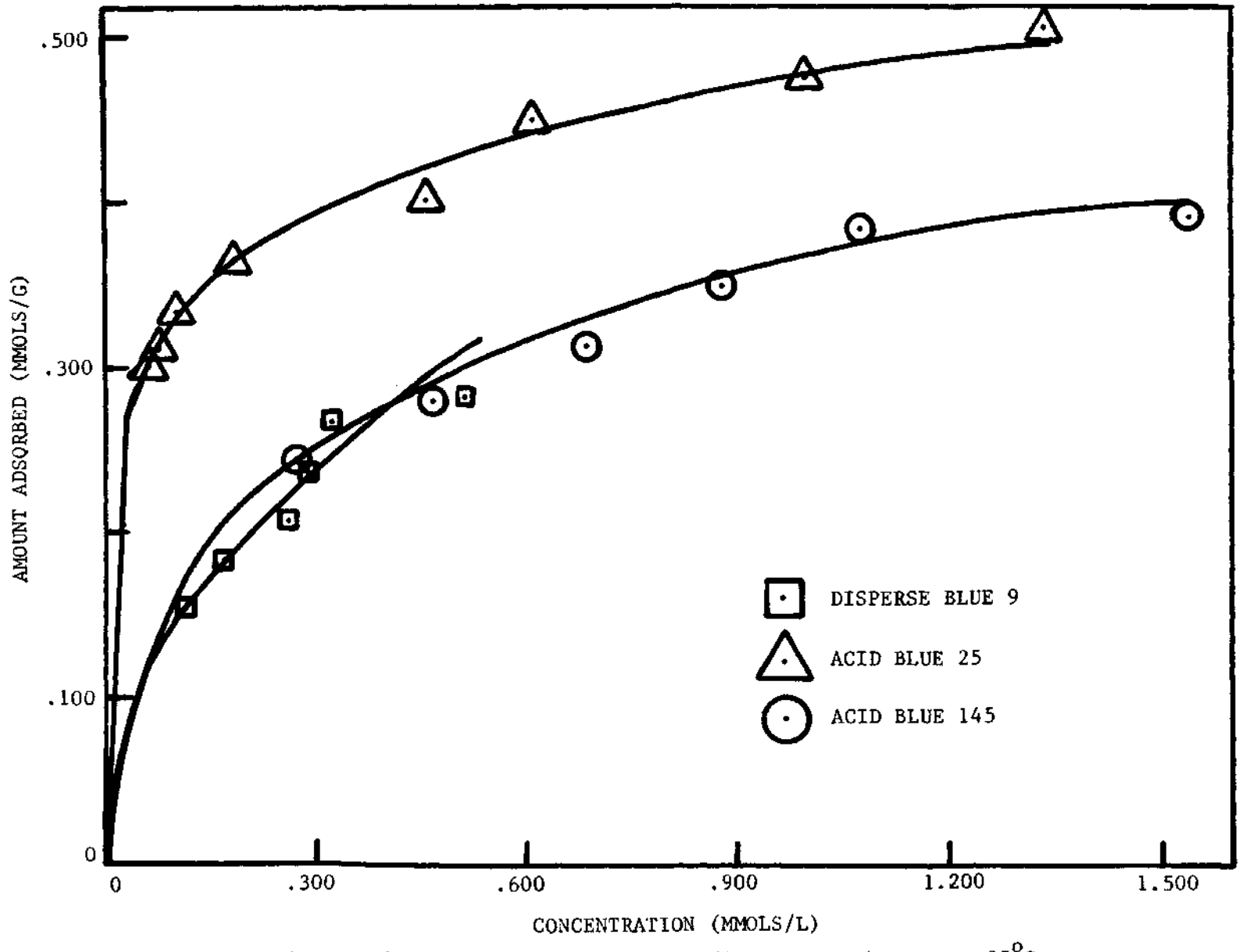


Figure 18. Isotherms of Impure Dyes in 75/25 Methanol/Water at 25°C

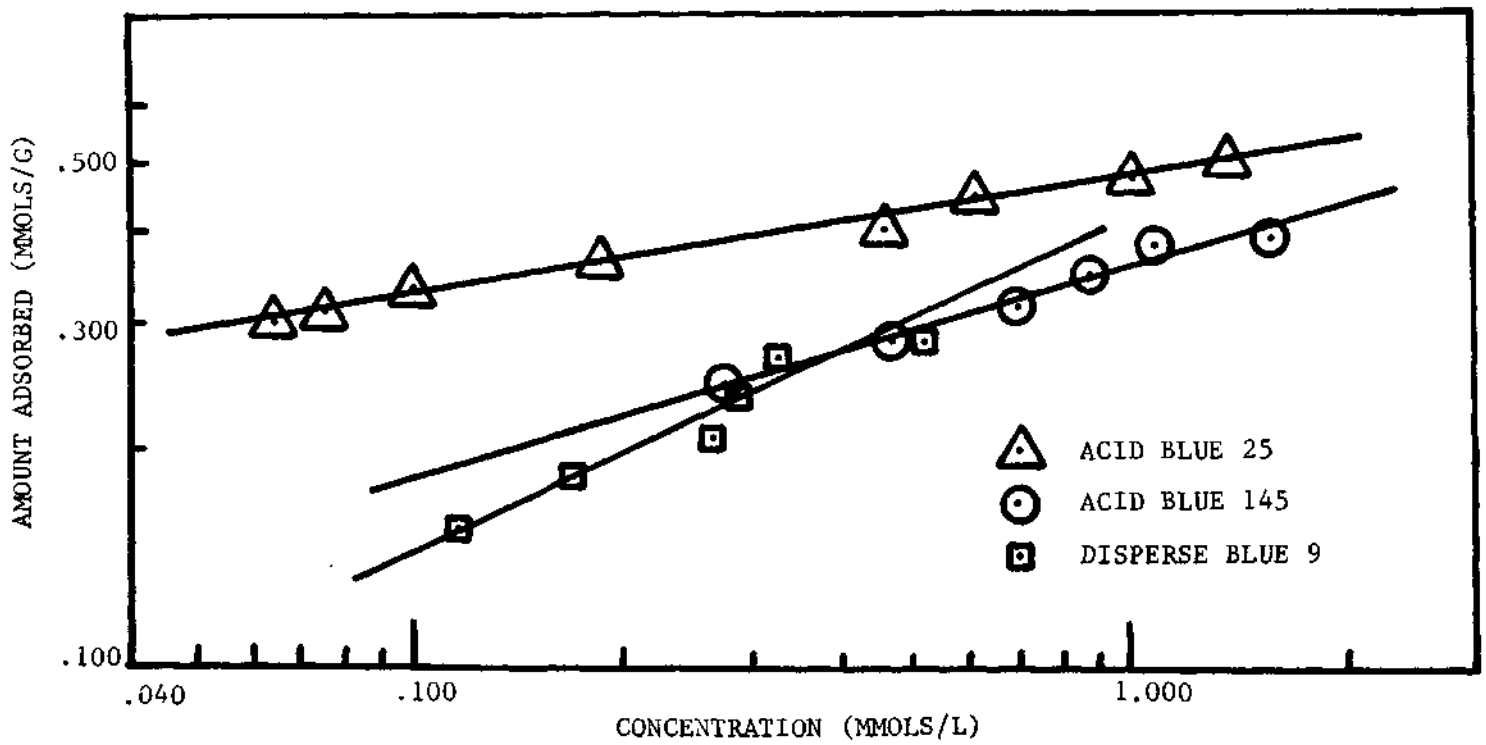


Figure 19. Isotherms of Impure Dyes in 75/25 Methanol/Water at 25°C

that Acid Blue 145 was adsorbed to a greater extent than the disperse dye at lower concentrations and the reverse was true at higher concentrations. The disperse dye was adsorbed to a much greater extent in this solvent than in water because more dye molecules were actually in solution and capable of entering the pore structure of the carbon.

In the alcohol/water solution in the concentration ranges examined it appears that the monosulfonated dye was absorbed to the greatest extent with the disulfonated and non-sulfonated dyes adsorbed to about the same extent but markedly less than Acid Blue 25. The effects of impurities in the commercial dyes again cloud the picture.

Temperature Effects

Comparisons of isotherms at 25°C and 50°C showed the effects of an elevation in temperature on adsorption.

Figures 20 and 21 show the effects of an elevation in temperature on the adsorption of impure Disperse Blue 9 from 75/25 methanol/water. The adsorption at the higher temperature was consistently more complete, but the effect was greater at the low concentrations than at the higher concentrations.

The results with Acid Blue 25 and Acid Blue 145 are similar (Figures 22, 23, 24, and 25). The elevated temperature increases the extent of adsorption from water consistently at all concentrations of dye in solution.

The reciprocal plots of the adsorption-time curves at 25°C and 50°C for the acid dyes in water and the Disperse Blue 9 in 75/25 methanol/water (Figures 40, 41, and 43) are helpful in explaining the greater adsorptions at the higher temperature. The increased adsorption

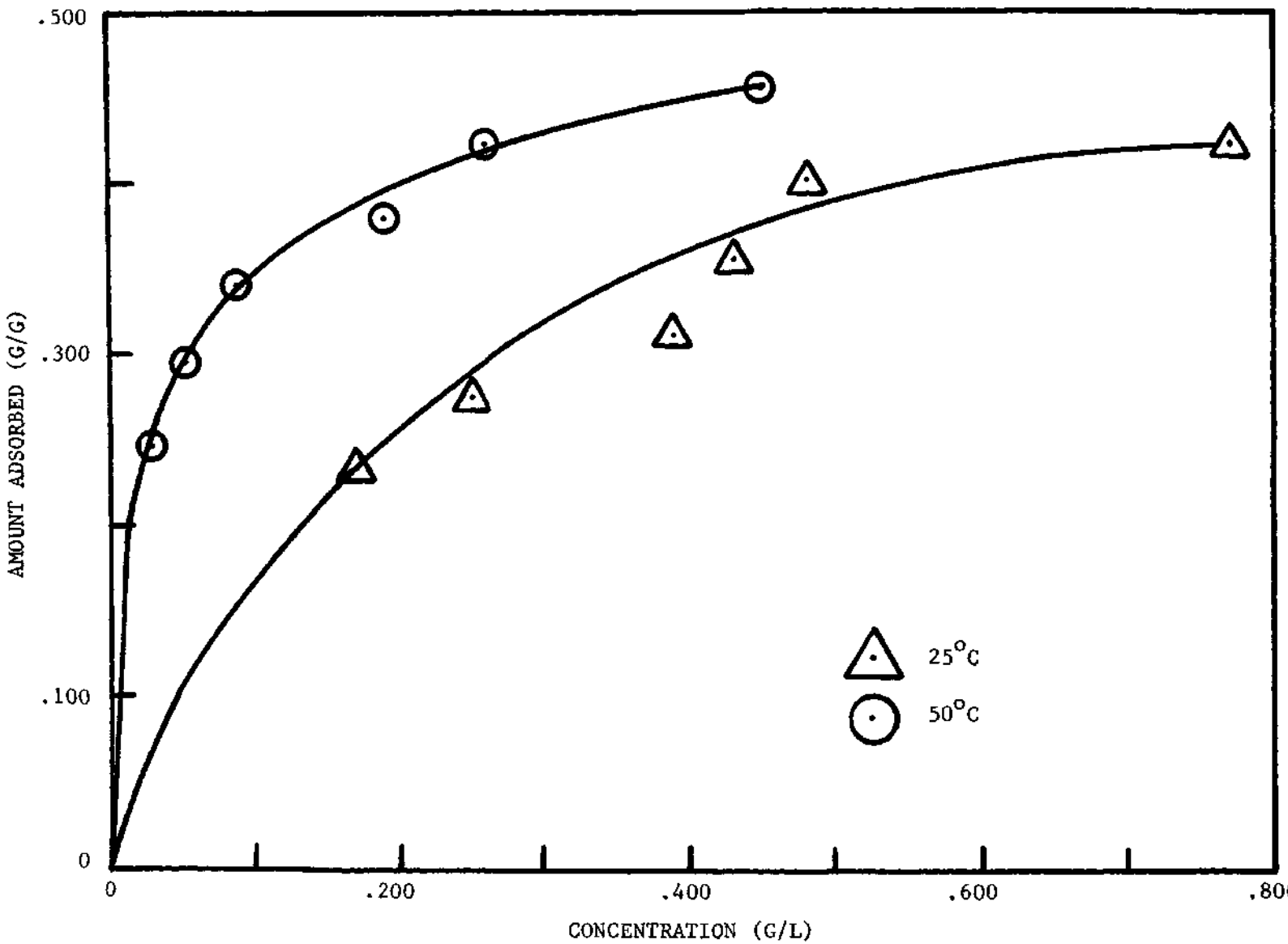


Figure 20. Isotherms for Impure Disperse Blue 9 in 75/25 Methanol/Water at 25°C and 50°C

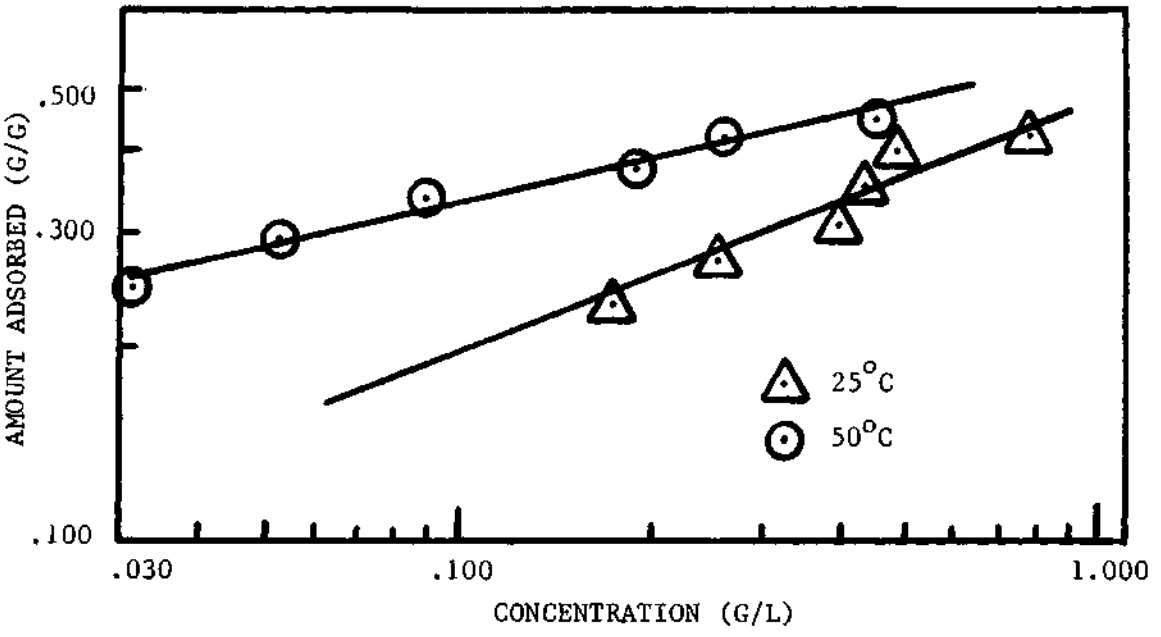


Figure 21. Isotherms for Impure Disperse Blue 9 in 75/25 Methanol/Water at 25°C and 50°C

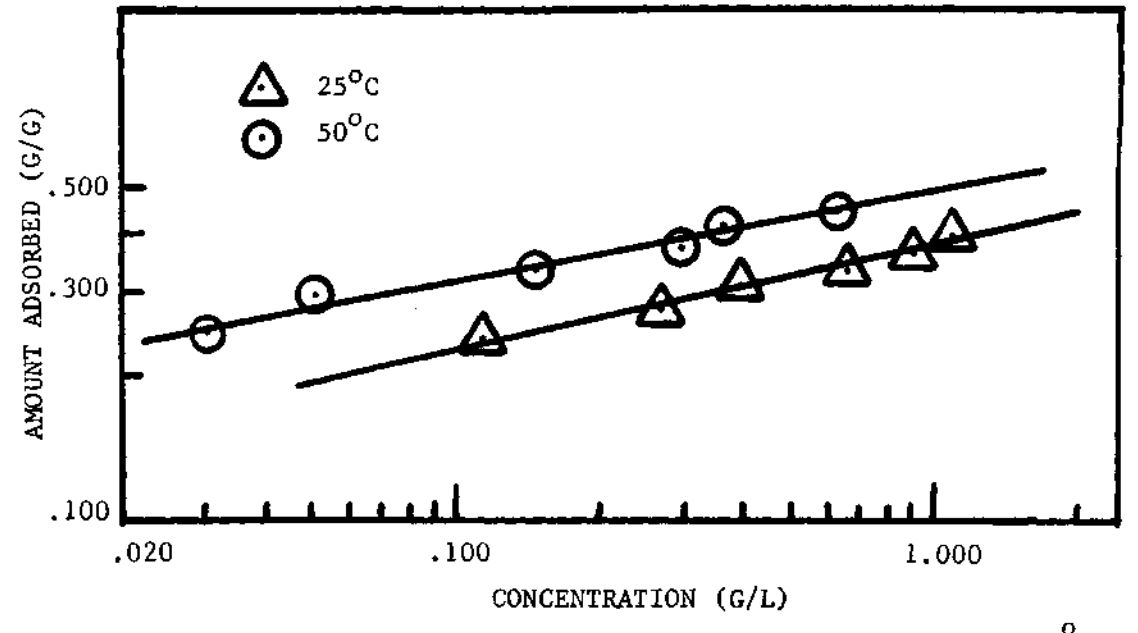


Figure 22. Isotherms for Impure Acid Blue 25 in Water at 25°C and 50°C

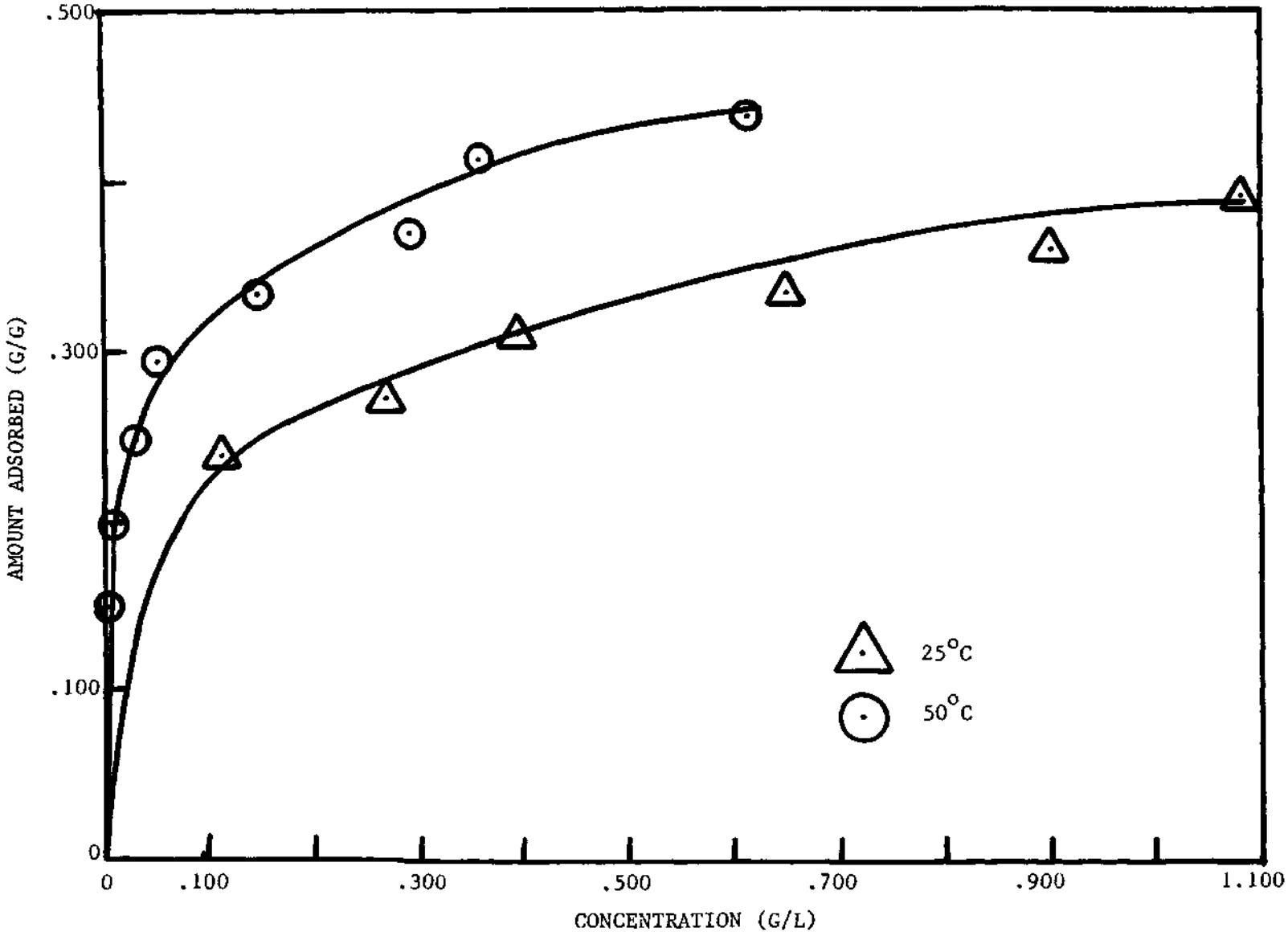


Figure 23. Isotherms for Impure Acid Blue 25 in Water at 25°C and 50°C

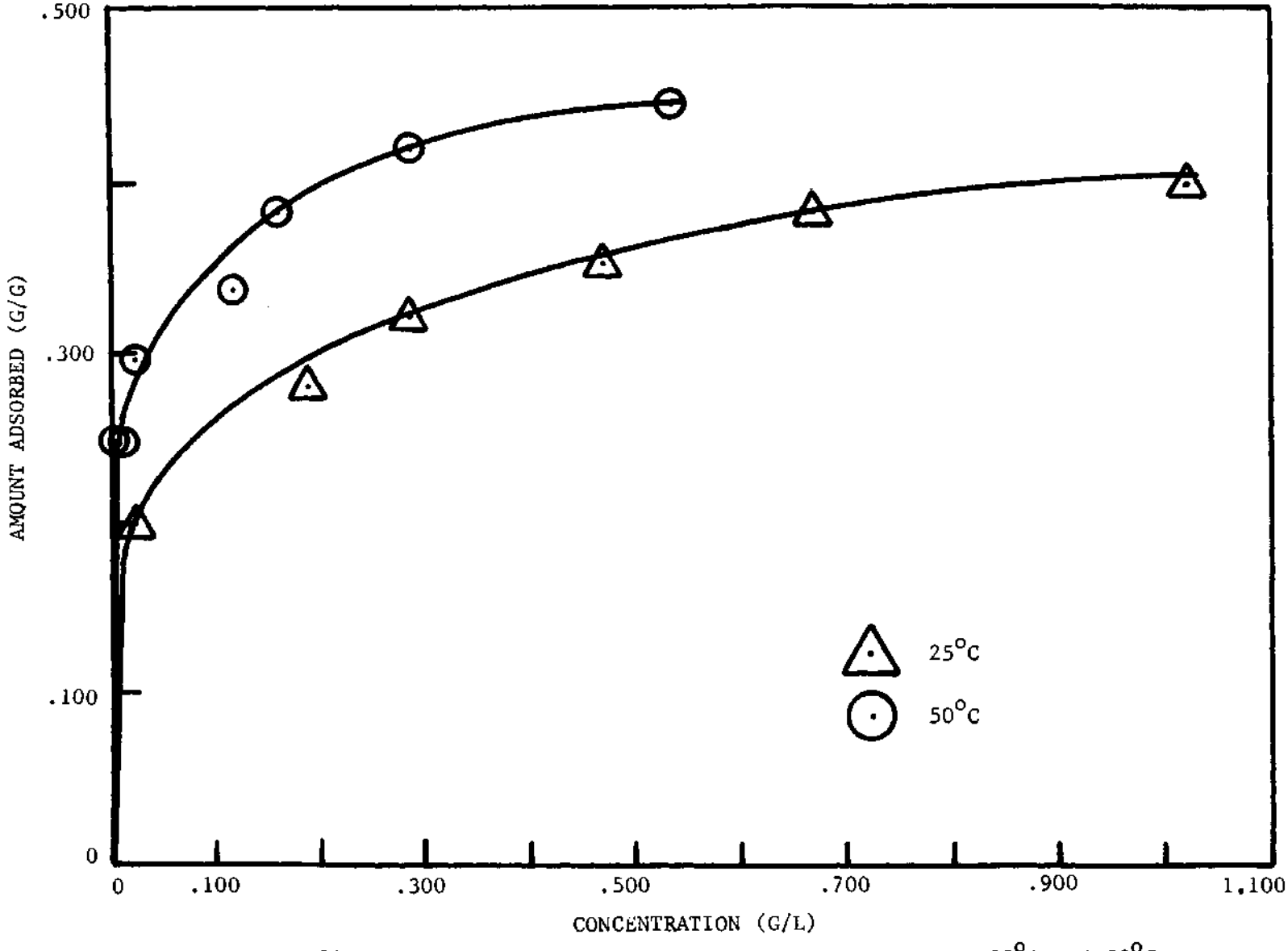


Figure 24. Isotherms for Impure Acid Blue 145 in Water at 25°C and 50°C

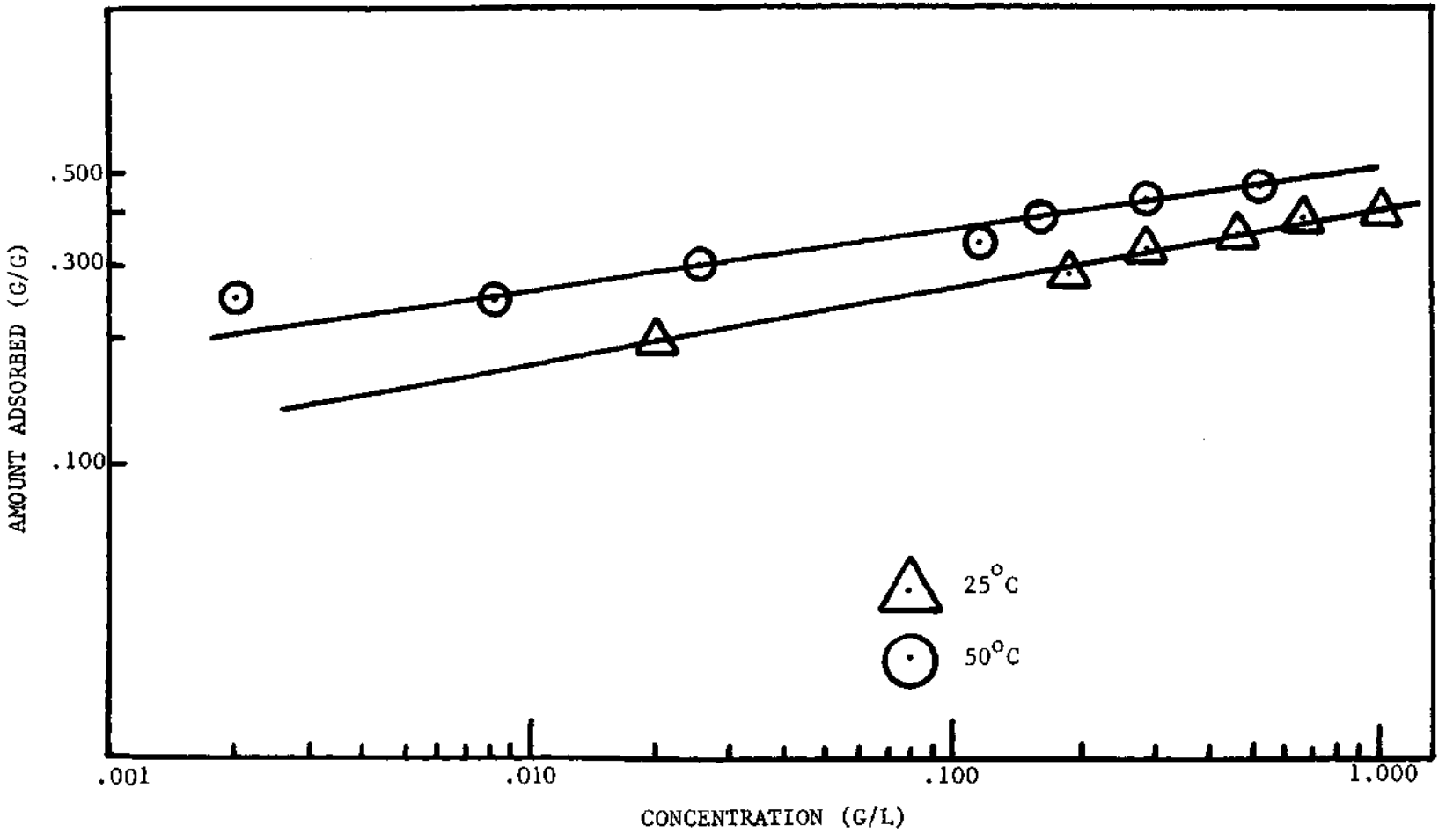


Figure 25. Isotherms for Impure Acid Blue 145 in Water at 25°C and 50°C

of both acid dyes is the result of an increased adsorption rate at 50°C, since Figures 40 and 41 show curves for the two temperatures converging at approximately the same equilibrium values. The increased adsorption of the Disperse Blue 9 at 50°C may be attributed, at least partially, to a greater equilibrium adsorption at 50°C, since reciprocal curves at the two temperatures (Figure 43) are nearly parallel and do not converge at the same equilibrium adsorption value.

pH Effects

The pH values for the dye solutions used in the evaluation of pH variation on adsorption varied slightly with the concentration of dye in solution. pH values given are averages for the dye solutions prior to the addition of carbon. None of the samples varied in pH by more than two tenths of a pH unit from the average for all concentrations of dye. Often, the deviations from the average were less than this. The three types of solutions of Acid Blue 25 had average pH values of 1.9, 6.6, and 10.3. The values for Acid Blue 145 solutions were 2.1, 6.8, and 10.6.

The data for Acid Blue 25 shown in Figures 26 and 27 show that as the pH is lowered, the adsorption at equilibrium increases. The differences between the neutral and basic pH curves begin to narrow at lower concentrations and at a low concentration in solution the adsorption for the basic pH appears to exceed that at the neutral pH.

The data for Acid Blue 145, found in Figures 28 and 29 is similar to that for Acid Blue 25, although the differences do not seem to be as pronounced. The isotherms show increased adsorption as pH is decreased. The difference between the acidic and neutral pH isotherms

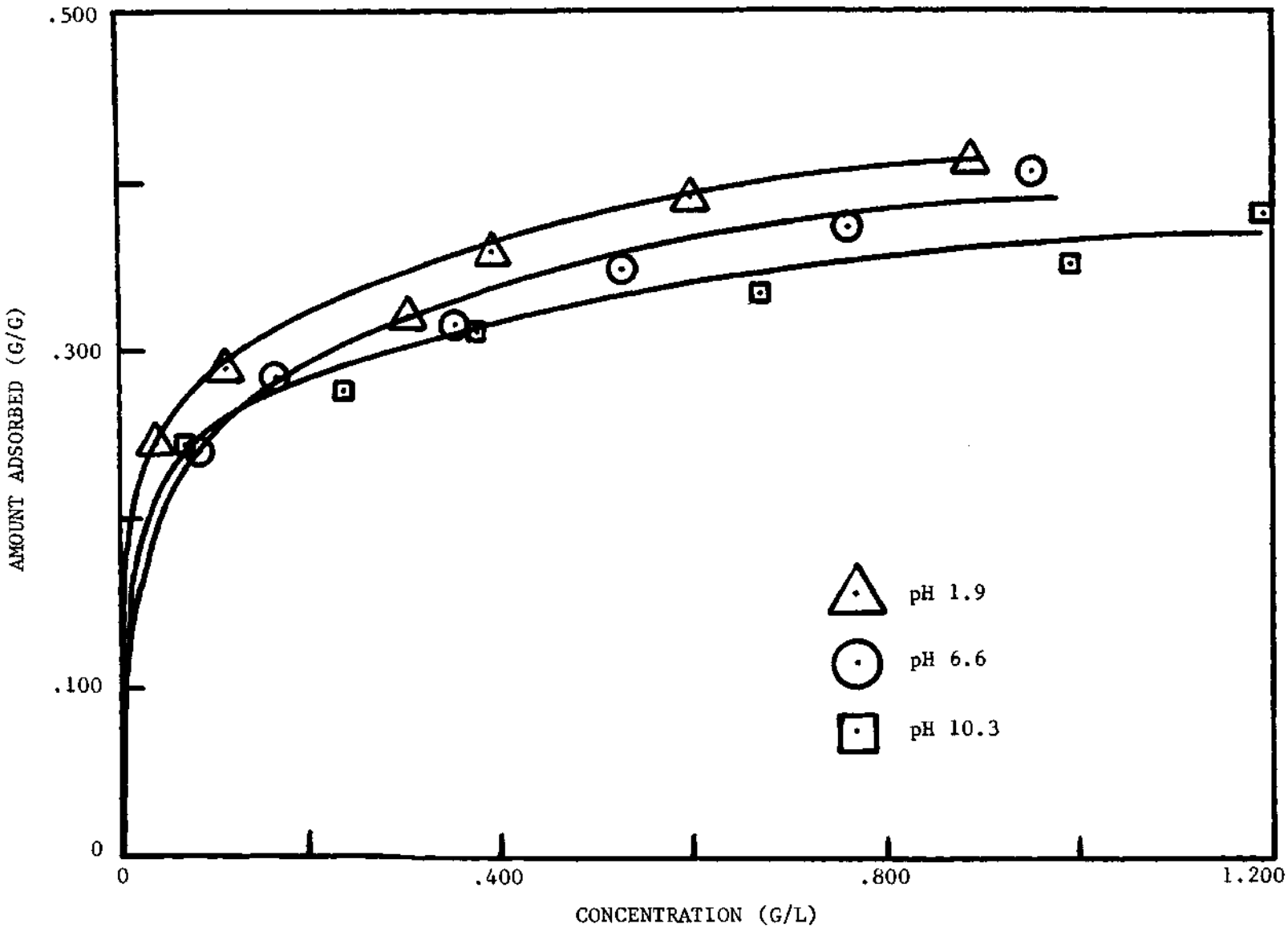


Figure 26. Isotherms for Impure Acid Blue 25 at Three pH Levels

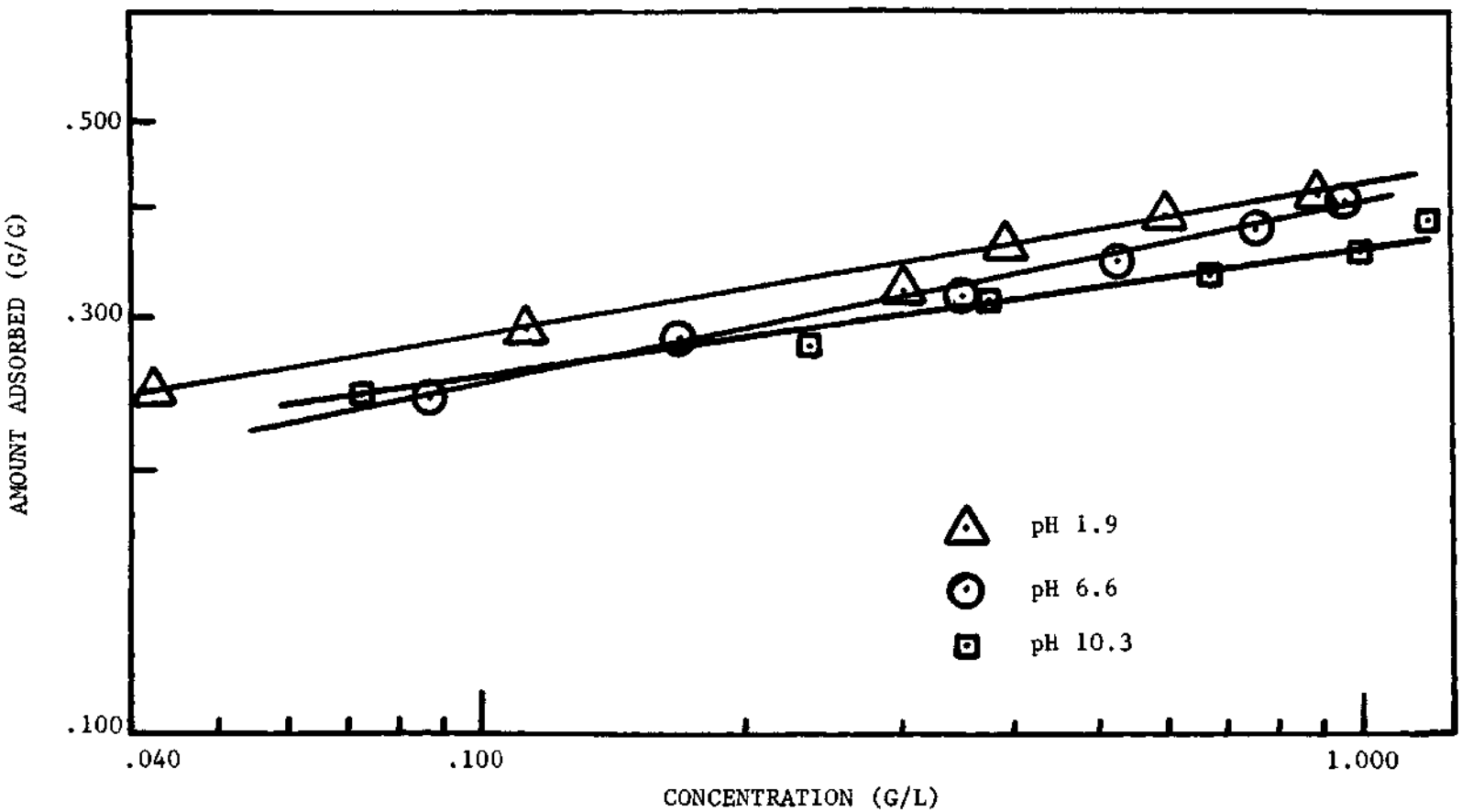


Figure 27. Isotherms for Impure Acid Blue 25 at Three pH Levels

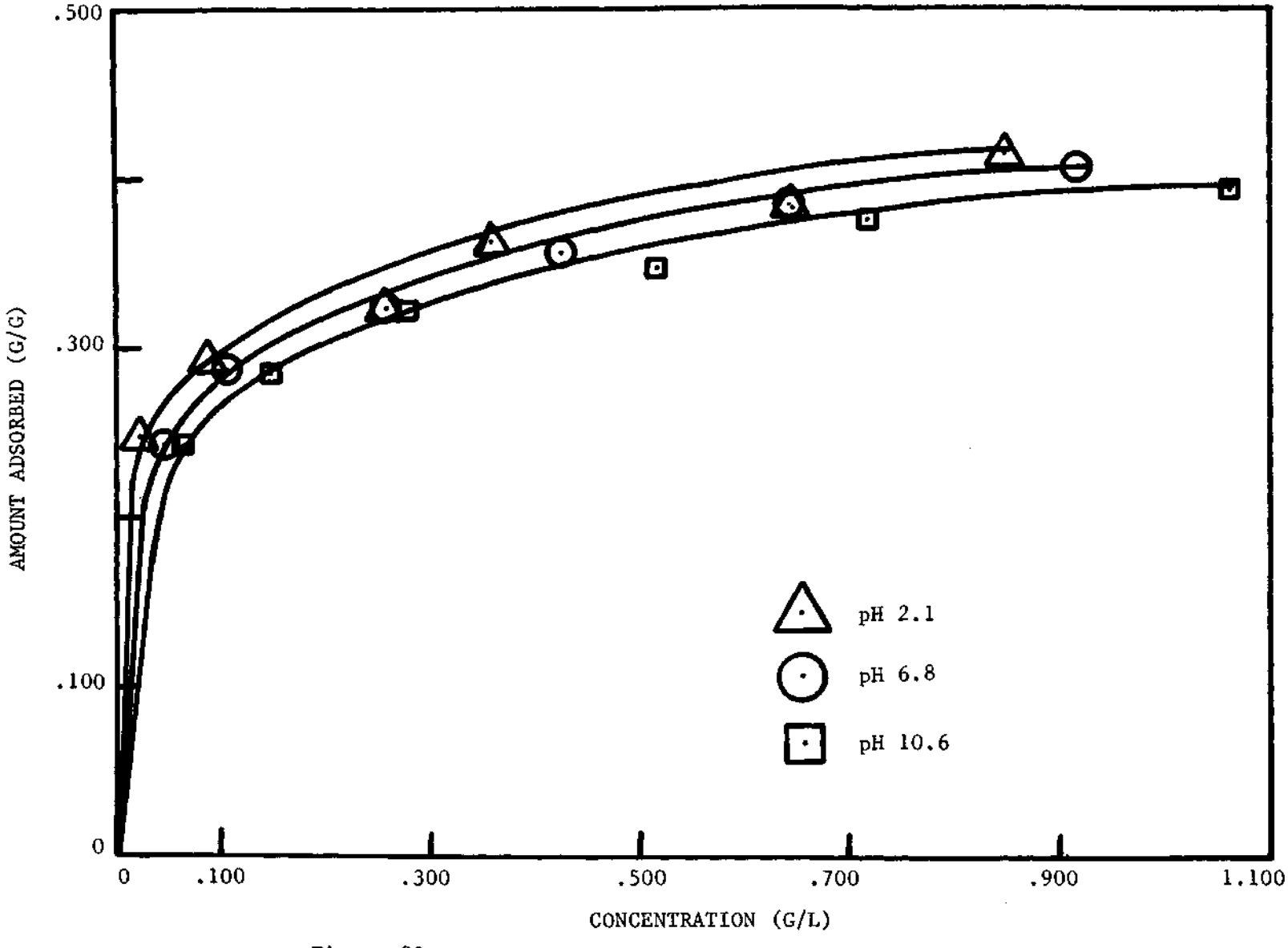


Figure 28. Isotherms for Impure Acid Blue 145 at Three pH Levels

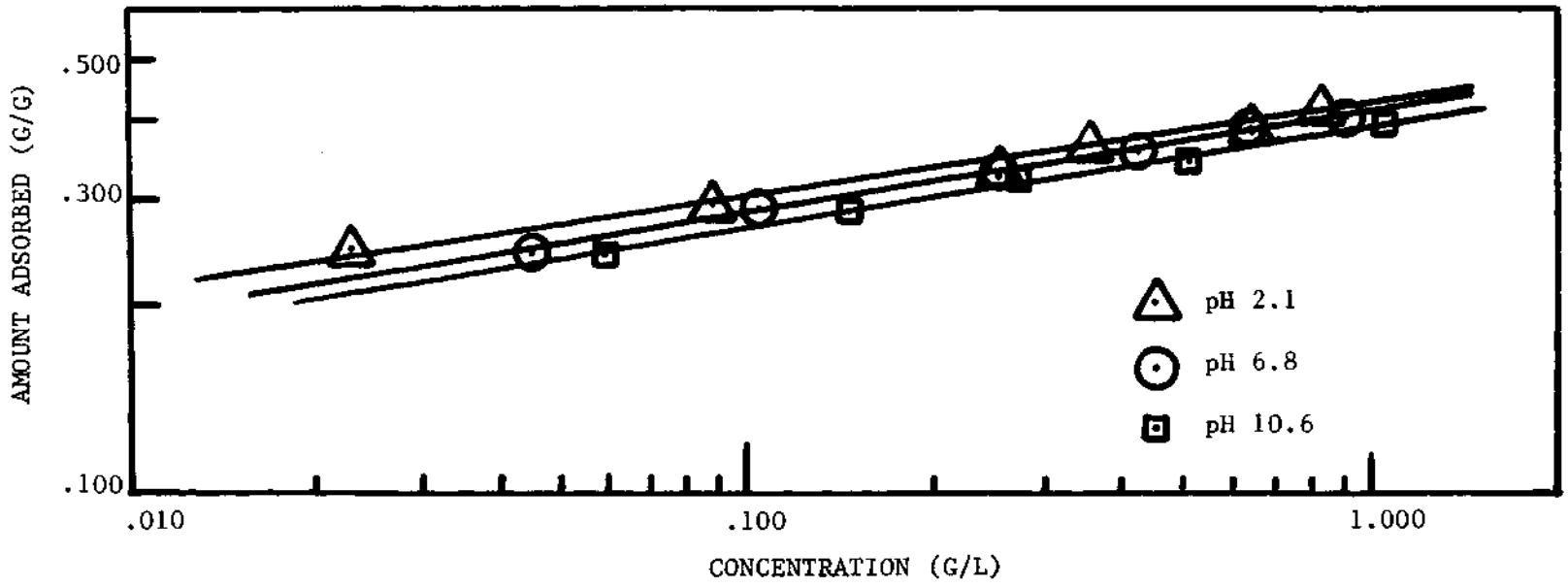


Figure 29. Isotherms for Impure Acid Blue 145 at Three pH Levels

appears to narrow somewhat at higher dye concentrations.

The results in these pH variation experiments are consistent with the results of Grollman (14) and Yajnik (12) who worked on the relation between pH and the adsorption of dyes containing sulfonic acid groups in their molecular structure. As the pH is decreased the amount of the un-ionized form of the dye is increased and dye molecules can be adsorbed on the carbon without a build up of negative charge, as mentioned by Hassler (17). Another factor which may be contributing to the increase adsorption at low pH is the cancelling of negative charge on the carbon surface by higher concentrations of hydrogen ions as noted by Porter (24). The decreased pH also affects the solute-solvent affinity by reducing the amount of the ionized form of the dye, thereby reducing the solubility of the dye in water and enhancing the adsorption.

Electrolyte Effects

The results for tests with Acid Blue 25 at high sodium sulfate concentration are not considered because the solubility of the dye was so greatly reduced by this high salt concentration that it is impossible to assess how much dye was adsorbed on carbon and how much just precipitated from solution.

Figures 30 and 31 are comparisons of the isotherms of impure Acid Blue 145 and Acid Blue 145 with 5.0 g/l added sodium sulfate in water at 25°C. The presence of the high concentration of salt increases the degree of adsorption with the effect apparently greater at lower concentrations of dye in solution. It is possible that the electrolyte helps to reduce the charge accumulating on the carbon as the

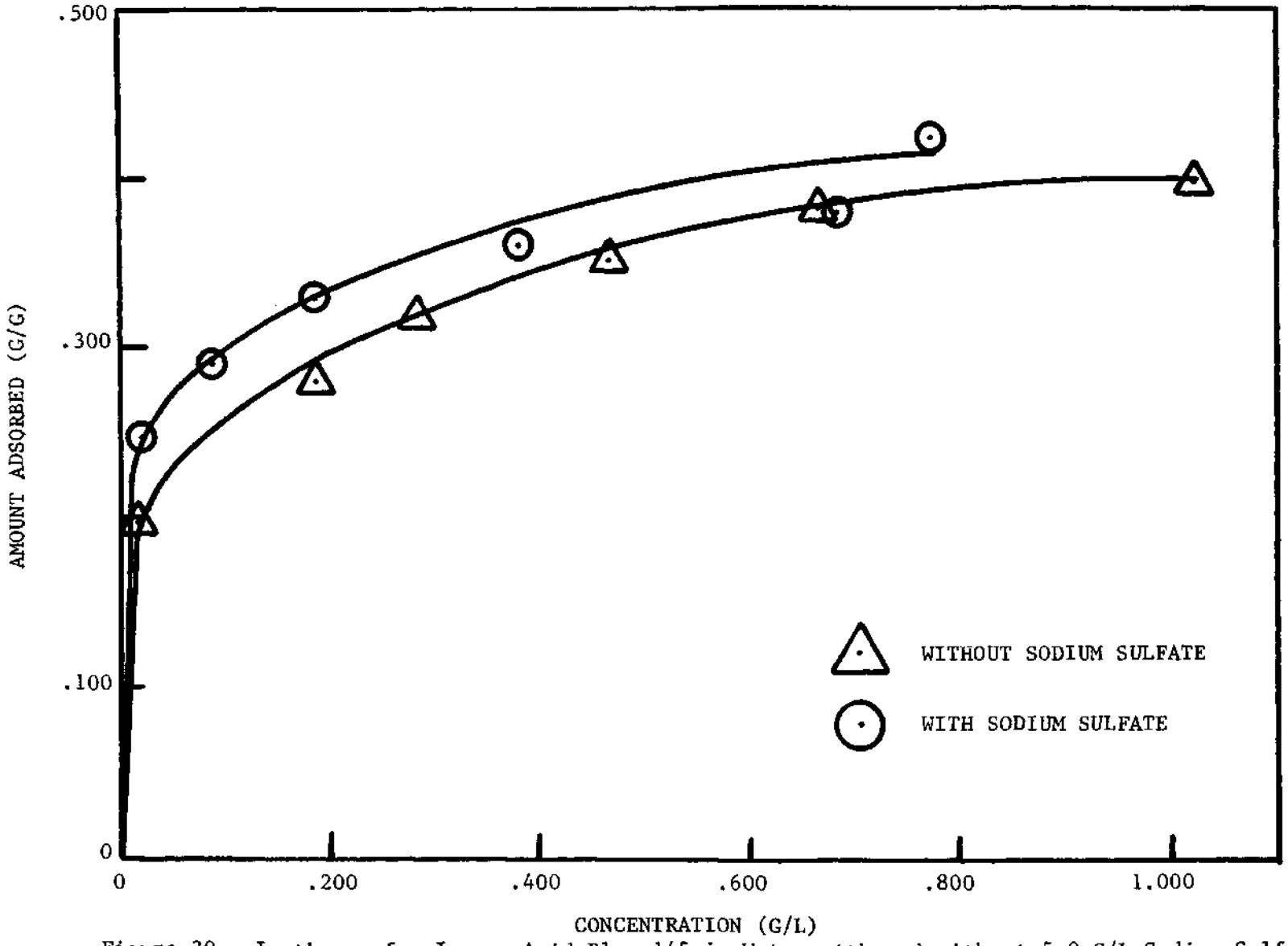


Figure 30. Isotherms for Impure Acid Blue 145 in Water with and without 5.0 G/L Sodium Sulfate

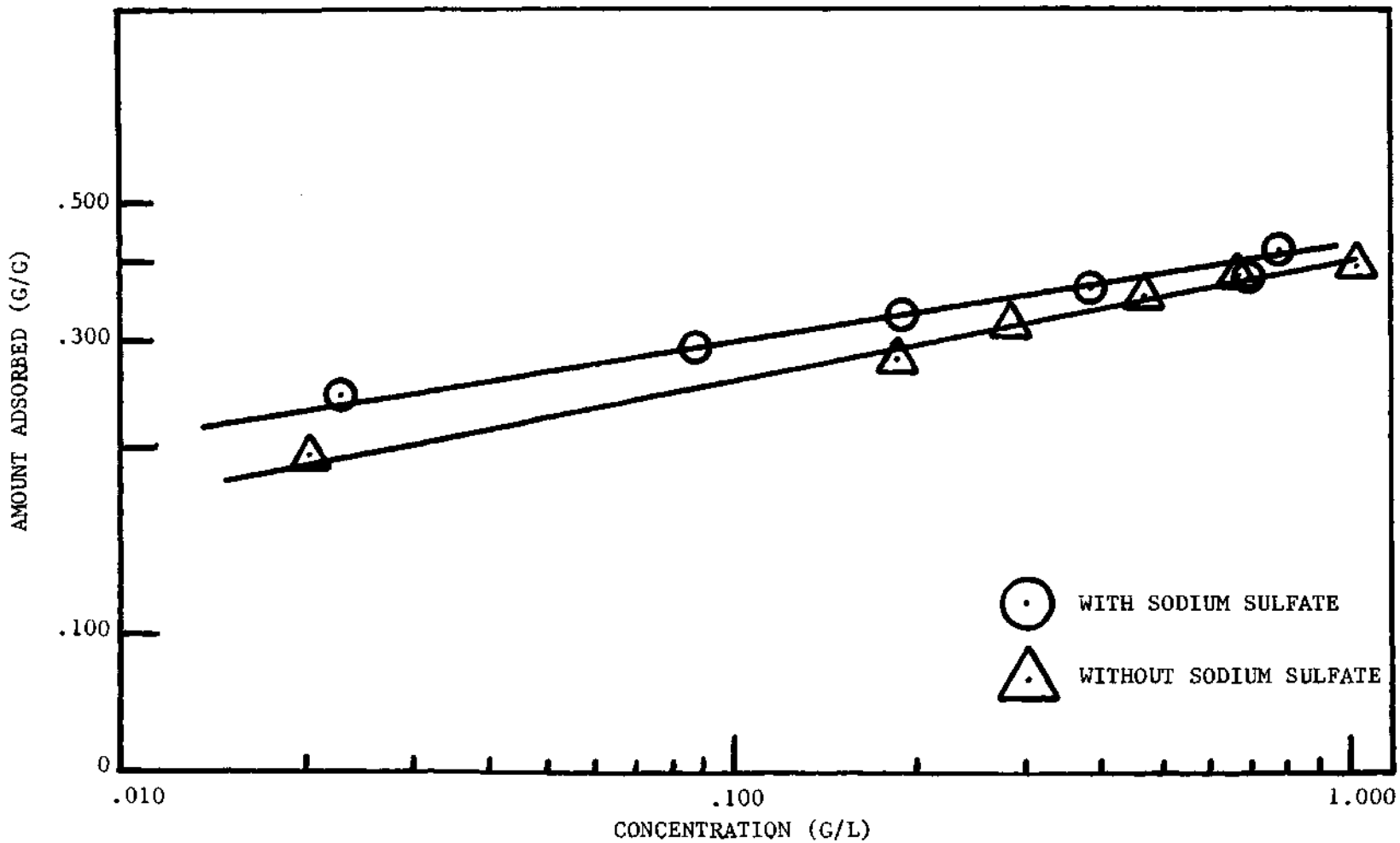


Figure 31. Isotherms for Impure Acid Blue 145 in Water with and without 5.0 g/l Sodium Sulfate

anionic dye is adsorbed, as predicted by Porter (24). Also, the high salt concentration probably reduces the solubility of the dye and improves the adsorption by this reduction of solute-solvent affinity.

Surfactant Effect

The spectrum of the 100 g/l solution of impure Igepon T showed absorbance values of 0.196 at 675 nm and 0.272 at 602 nm which is the wavelength of the maximum peak for Acid Blue 145. Since the concentration of the Igepon T in experiments with Acid Blue 145 did not exceed 7.5 percent of the concentration of the surfactant solution analyzed, and since the dye solutions were diluted a minimum of 25 times before analysis, the contribution of the surfactant to the absorbance values of dye solutions was considered negligible. The standard correction for background was applied to the solutions, and this would eliminate small contributions of the surfactant to absorbance values.

Figures 32 and 33 illustrate the effect of the presence of Igepon T on adsorption of impure Acid Blue 145. The addition of 1.0 g/l of the active ingredient of Igepon T reduces the amount of adsorption of dye. The addition of a second gram per liter of surfactant further reduced the adsorption of dye but to a lesser extent than the first. The effects seem to be greatest at low dye concentrations in solution.

The surfactant is probably adsorbed on the carbon and competes with dye molecules for positions on the carbon surfaces. Since Igepon T is an anionic surfactant, accumulation of surfactant on the carbon could give the carbon a more negative charge and inhibit the approach of the anionic dye molecules.

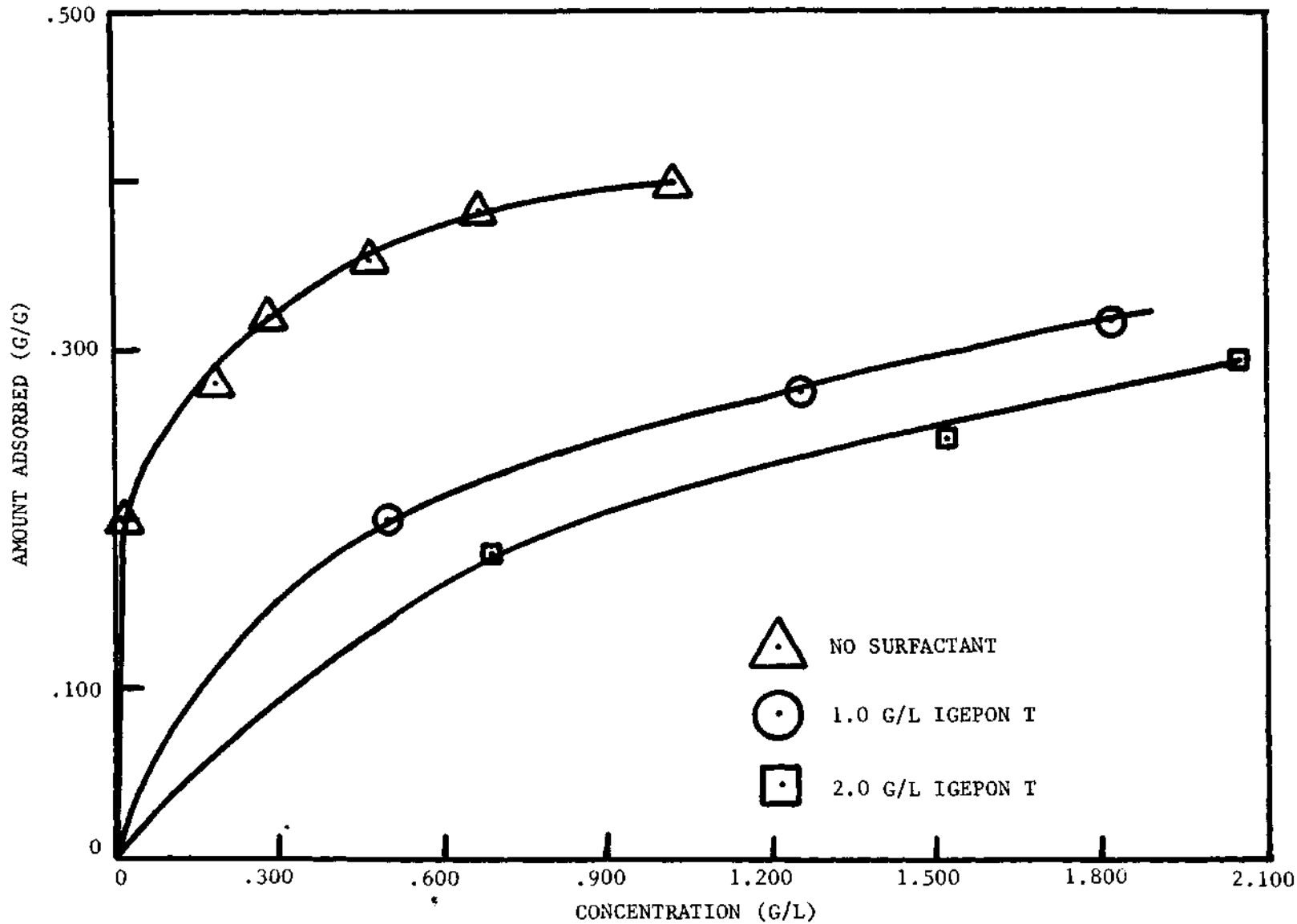


Figure 32. Isotherms for Impure Acid Blue 145 in Water with Varying Amounts of Igepon T

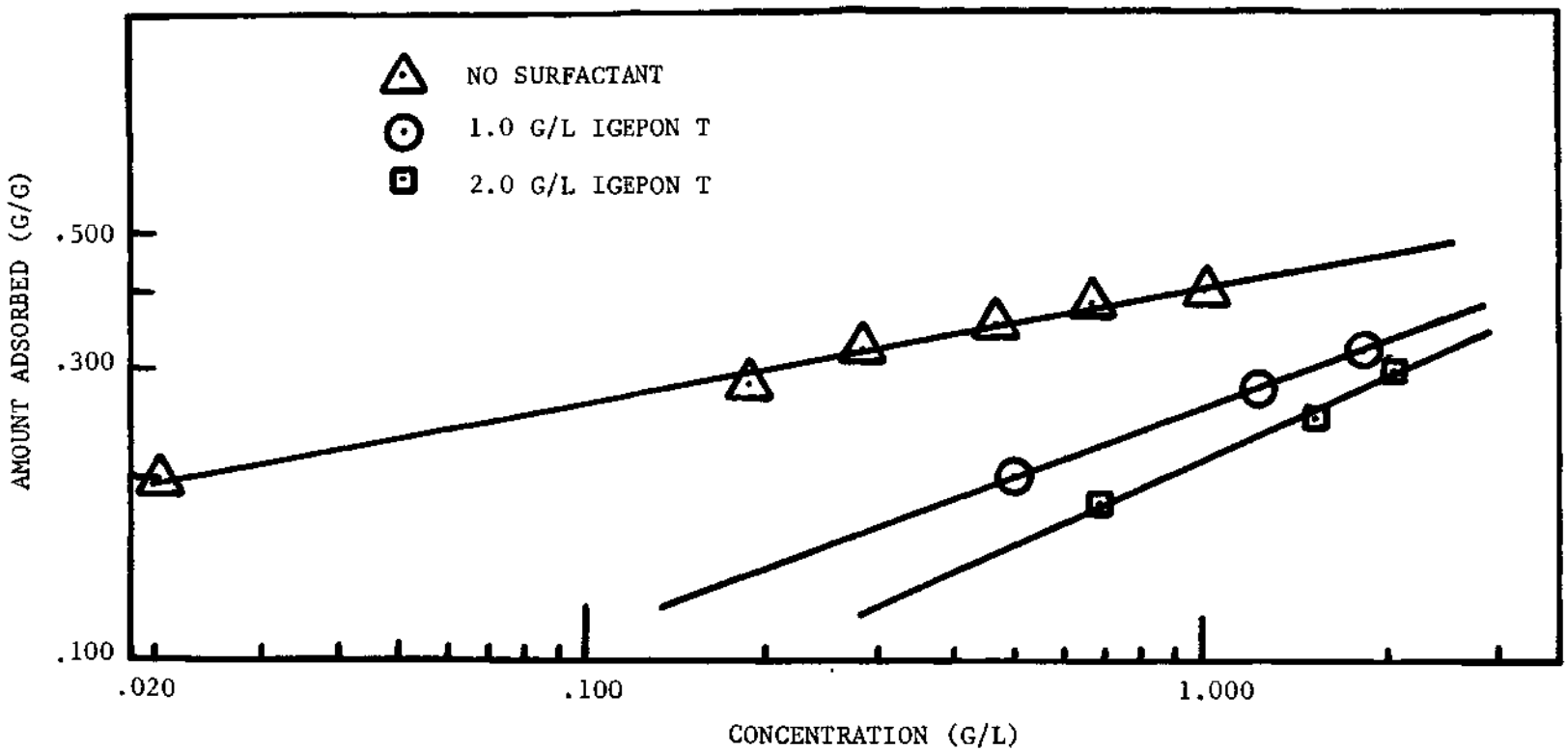


Figure 33. Isotherms for Impure Acid Blue 145 in Water with Varying Amounts of Igepon T

The effects observed are attributed to the surfactant and not to impurities in the surfactant. The impurities in the surfactant are probably inorganic salts and the effect of one inorganic salt, sodium sulfate, has already been shown to slightly increase the adsorption of Acid Blue 145, rather than decrease it as in this experiment with surfactant.

Solvent Effects

Figures 34 and 35 compare isotherms for impure Disperse Blue 9 at 25°C from water and from 75/25 methanol/water. The adsorption from the alcohol/water solution is much greater due to the greater number of molecules actually in solution in the alcohol/water rather than in dispersion as in the water.

The adsorption of impure Acid Blue 25 from the two types of solvents at 25°C is compared in Figures 36 and 37. The isotherms are closely similar with the adsorption from water slightly less than that from 75/25 methanol/water.

Figures 38 and 39 show the isotherms for the adsorption of impure Acid Blue 145 from the two solvents. Adsorption is better from water with the difference decreasing at higher concentrations of dye in solution.

The effects of the different solvents on the adsorption of the acid dyes can probably be explained on the basis of differing solubilities of the dye in different solvents.

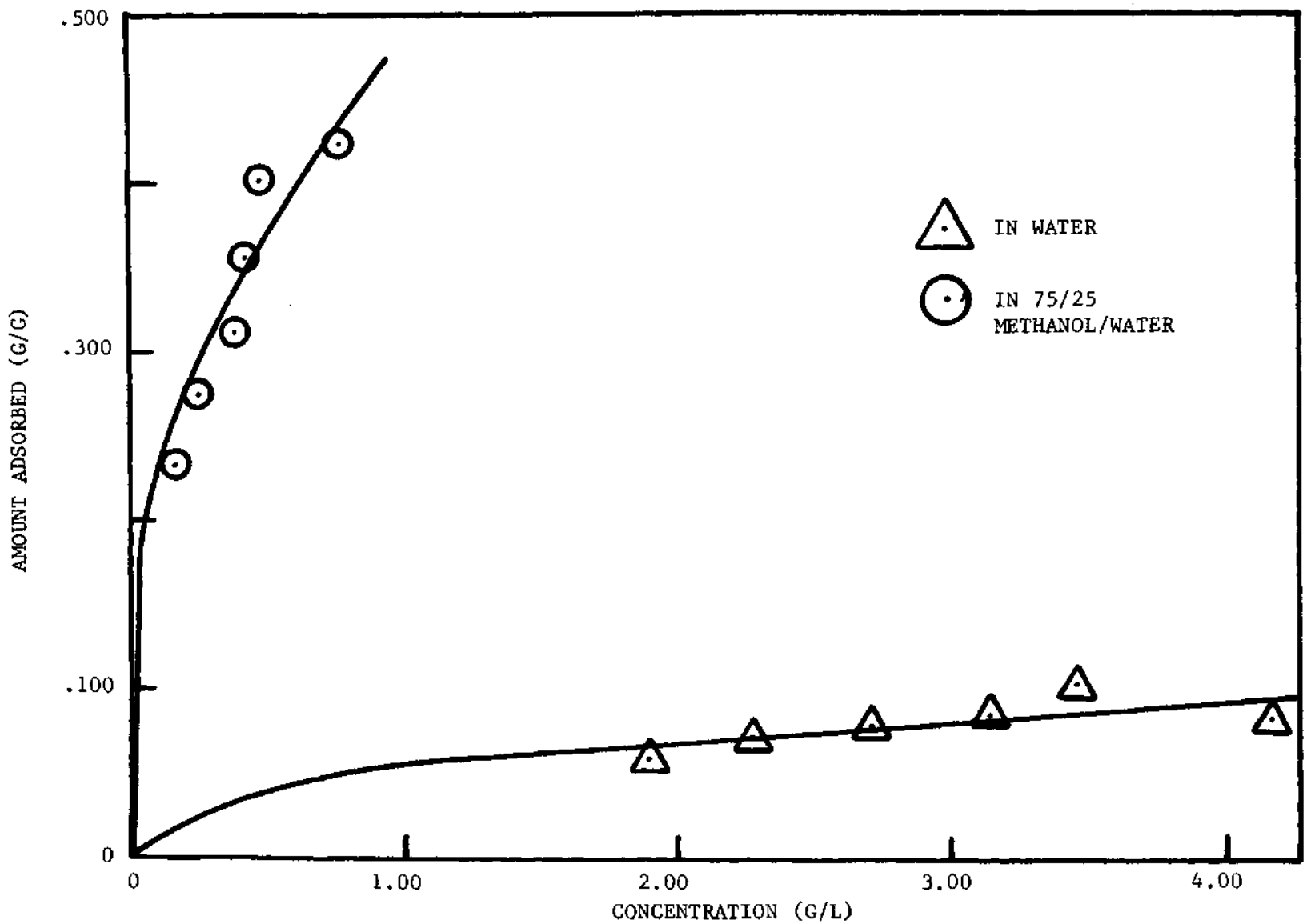


Figure 34. Isotherms for Impure Disperse Blue 9 in Different Solvents

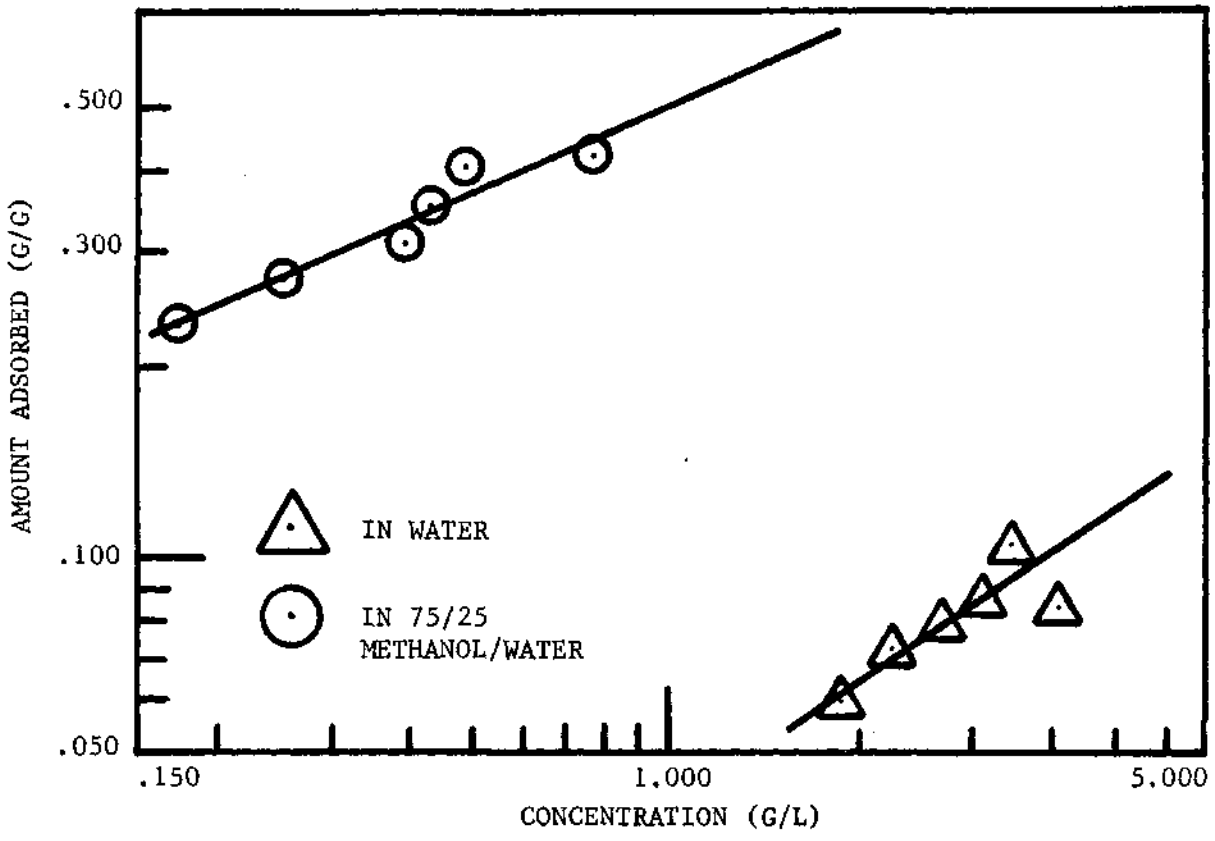


Figure 35. Isotherms for Disperse Blue 9 in Different Solvents

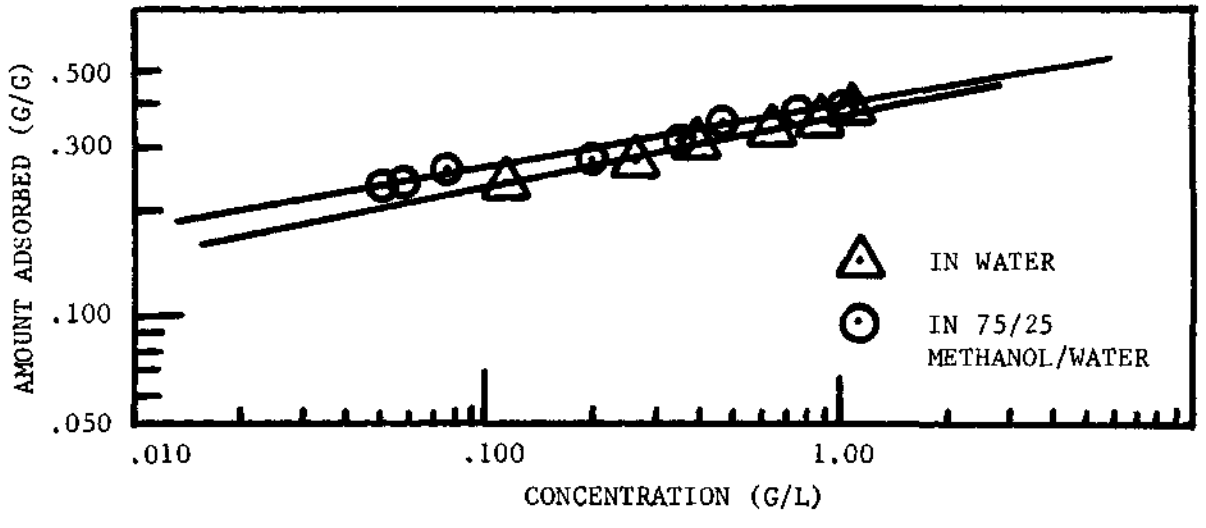


Figure 36. Isotherms for Impure Acid Blue 25 in Different Solvents

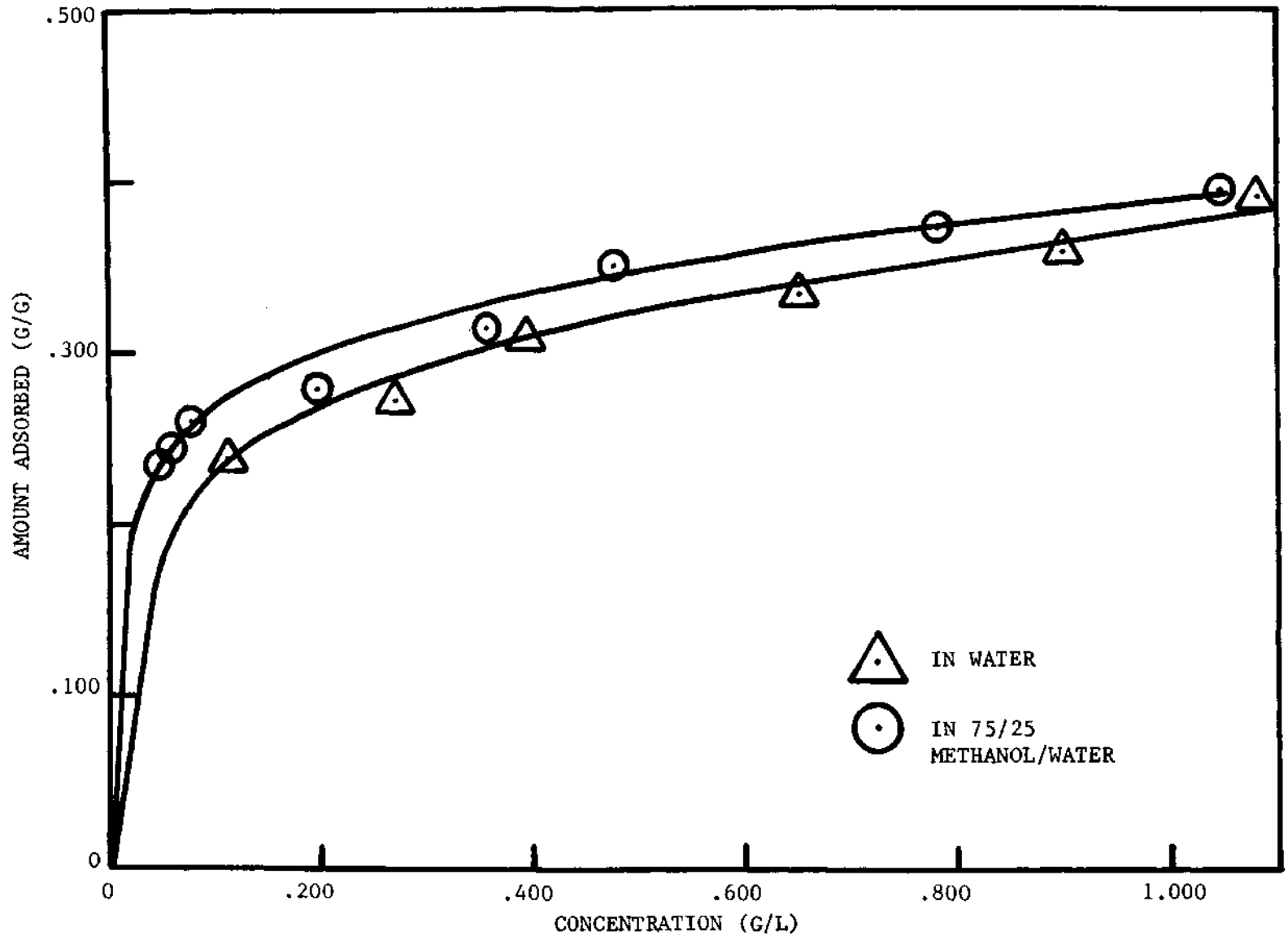


Figure 37. Isotherms for Impure Acid Blue 25 in Different Solvents

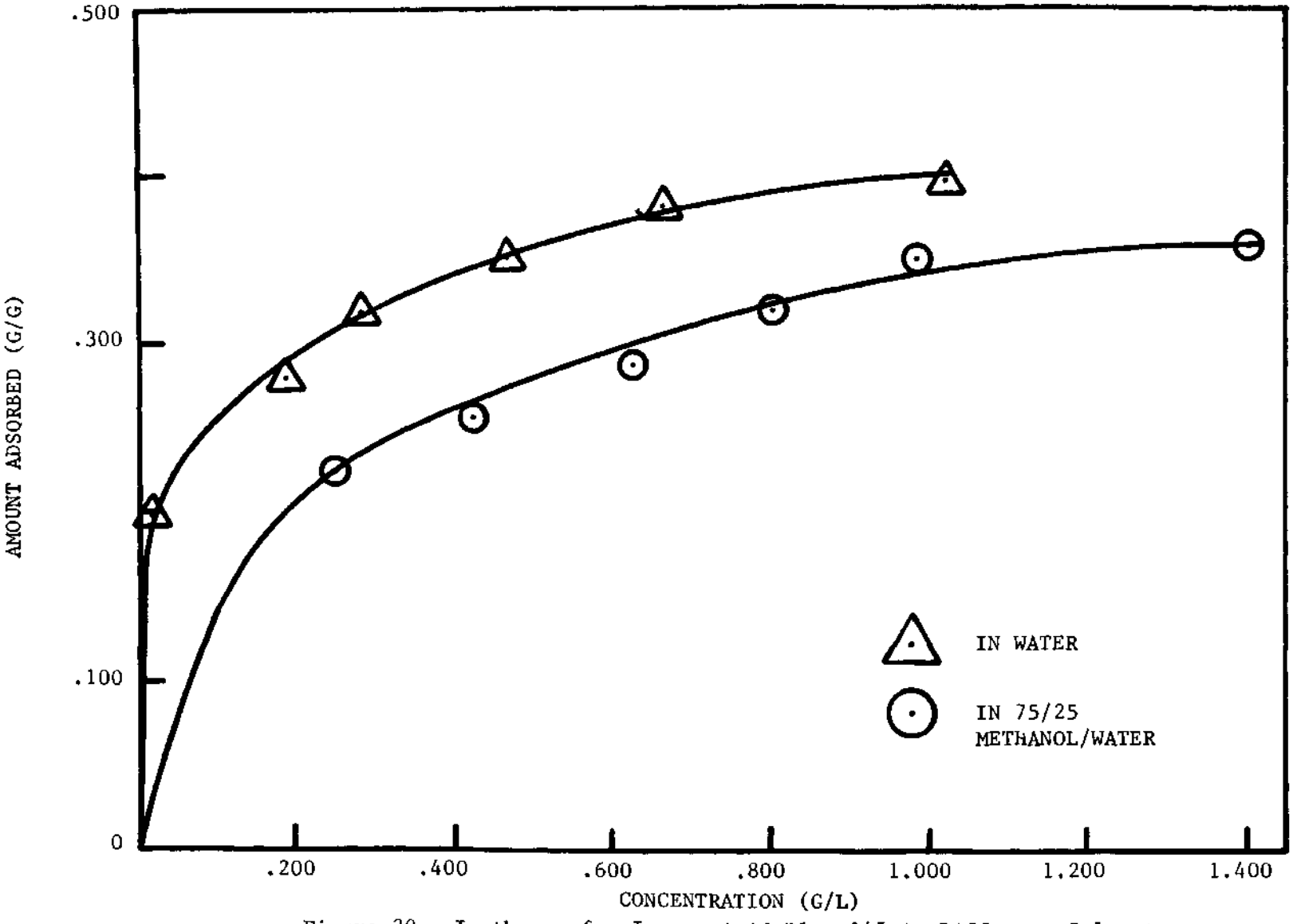


Figure 38. Isotherms for Impure Acid Blue 145 in Different Solvents

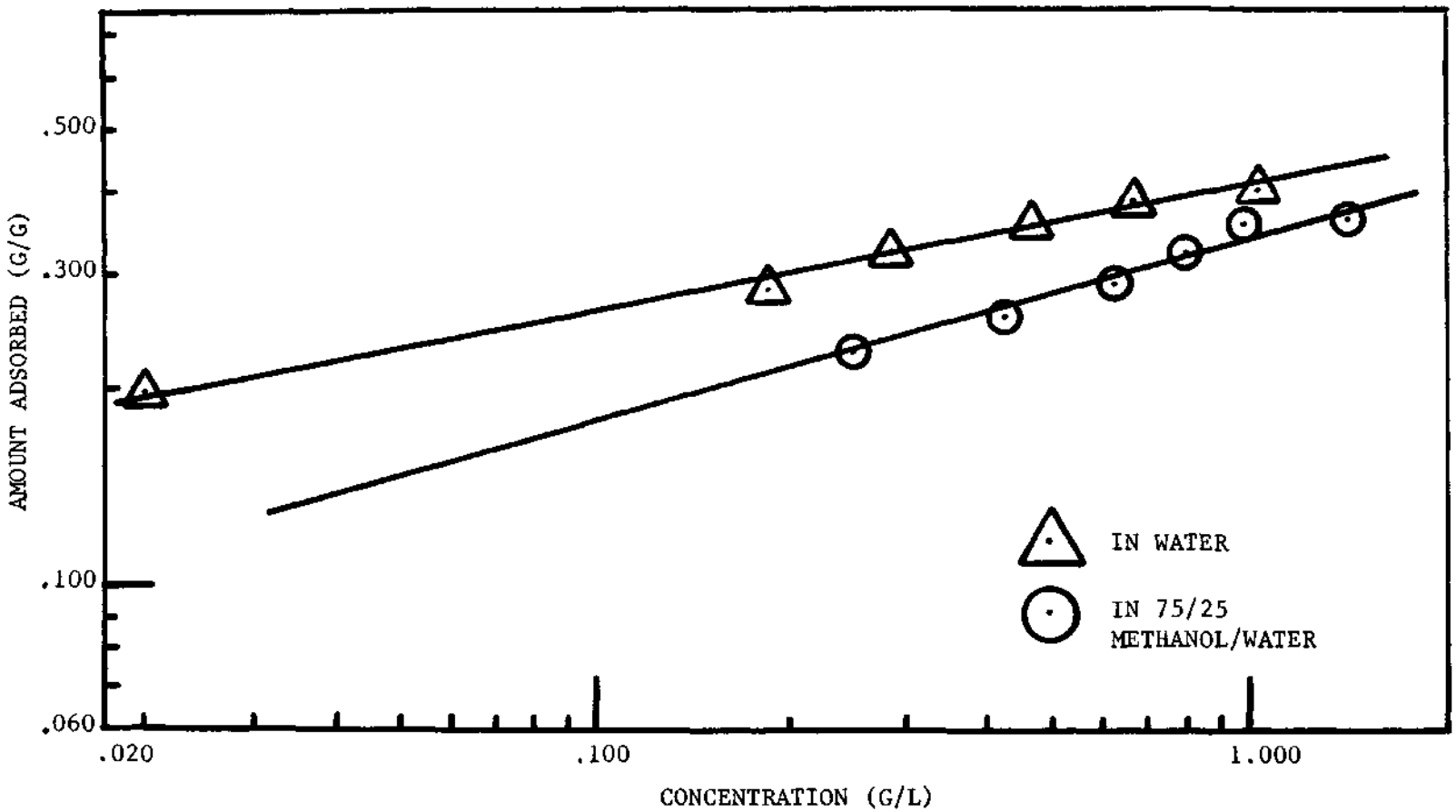


Figure 39. Isotherms for Impure Acid Blue 145 in Different Solvents

CHAPTER V

CONCLUSIONS

The introduction of a second sulfonic acid group onto a monosulfonated dye with an anthraquinone based structure results in decreased adsorption of the dye from water.

Variations in temperature, pH, electrolyte content and surfactant content of water solutions of anthraquinone based dyes affect the adsorption of dye by activated carbon. An increase in temperature increases the rate of adsorption of sulfonated anthraquinone dyes from water and increases the equilibrium adsorption of a non-sulfonated dye from a solution of methanol and water. A decrease in pH results in greater equilibrium adsorption of anthraquinone dyes containing sulfonic acid groups from water due to a reduction in ionization of the acid groups and a resultant reduction in solubility, or a neutralizing of negative charge on the carbon. The presence of a large concentration of sodium sulfate shifts the equilibrium state toward more adsorption on carbon for a sulfonated anthraquinone dye. The presence of an anionic surfactant greatly decreases the adsorption of a sulfonated anthraquinone dye from water.

When the character of solvents is changed, adsorption of anthraquinone dyes by carbon is changed to a degree depending on the particular dye examined.

CHAPTER VI

RECOMMENDATIONS

When attempting to evaluate the effects of the molecular structure of a substance on its adsorption, more clear-cut results are obtained when purified specimens of the substance to be adsorbed are used. Impurities alter the adsorption of the substance under investigation, as evidenced in this work, and make assessment of structural effects more difficult.

Accurate data on the equilibrium conditions for an activated carbon adsorption system is valuable information for use in evaluating the effects of variable conditions on adsorption. Equilibrium conditions were not fully achieved in this work. Procedures which allow the establishment of true equilibrium conditions in a reasonable time would permit a more accurate assessment of effects of varying conditions on equilibrium states without the need to consider rate effects. The use of pulverized carbon gives information on true equilibrium conditions, if equipment for filtration of the small carbon particles from solution is available.

Examination of adsorption by activated carbon of anthraquinone dyes with chemically active groups other than sulfonic acid groups, and of dyes of other basic structural types under the varying conditions found in textile dyehouse wastewaters would contribute to the store of knowledge about removal of these wastes from solution, and would be of

value to those concerned with the development of waste treatment procedures for particular types of dye wastes.

APPENDIX A

Table 3. Properties of Nuchar WV-L Granular Activated Carbon*

Property or Specification	Value
Apparent Density (lb./cubic foot)	30
Surface Area (Nitrogen BET Method) (m^2/g)	1000
Particle Density, Wetted in Water (g/cc)	1.4
Effective Size (mm)	0.90
Uniformity Coefficient	1.80
Particle Size (U. S. Sieve Series)	8 x 30
Oversize (percent) Maximum	8
Undersize (percent) Maximum	5
Molasses Decolorizing Index, Minimum	6.3
Iodine Number, Minimum	950
Abrasion Number, Minimum	70
Moisture When Packed (percent), Maximum	2
Ash (percent), Maximum	7.5

*From Product Data Bulletin supplied by Westvaco.

APPENDIX B

CORRECTION OF ERRORS IN ABSORBANCE VALUES DUE TO CARBON CONTRIBUTION

Early attempts at correction of absorbance values for carbon contribution consisted of running blank solutions with carbon under the same conditions and for the same times as dye solutions. These blank solutions consisted of the solvent in which the dyes were dissolved. Blank solutions of distilled water and 75/25 methanol water were contacted with carbon with agitation in the constant temperature bath for various times at 25°C and 50°C. The blank solutions were filtered and examined spectrophotometrically in the same manner as the dye solution. The results showed negligible absorbance for these solutions and this method of evaluating the contribution of carbon to the absorbance values was abandoned.

The method of correction which was finally adopted involved the comparison of adsorption spectra for dye solutions which had been in contact with carbon to spectra of the same types of dye solutions which had not been in contact with carbon. The assumption was made and later substantiated that the contribution of carbon to the absorbance spectrum was relatively constant from 700 to 600 nm. This is the region in which the maximum peaks for all the dyes in all solutions were located. The substantiation came when a dilute solution (0.25 g/l) of Acid Blue 145 was run with one gram of carbon for 50 hours at 25°C. No blue color was visible in the filtered solution, and there was no peak at the expected wavelength when the absorbance spectrum

was run. The lack of blue color and lack of a peak indicated that practically all of the dye had been absorbed. The absorbance value between 700 and 600 nm was constant and was not zero as would have been expected if nothing were present in the solution. The absorbance in this region was almost one-tenth of an absorbance unit. This absorbance was attributed to the presence of something from the carbon.

Since the contribution by carbon to the absorbance values was assured to be constant between 600 and 700 nm, the amount of error in absorbance due to carbon could be mathematically accounted for by comparison of absorbance spectra of dye solutions contacted with carbon and those which were not. The spectra obtained in the calibration curve experiments were examined and ratios of the absorbance at the maximum peak to the absorbance at 675 nm were obtained. These ratios were seen to be equal or to vary slightly from concentration to concentration for each dye solution considered. The ratios of maximum absorbance to absorbance at 675 nm for many of the dye solutions contacted with carbon were found to be considerably lower than the ratios for the respective calibration spectra. This was particularly true for the Disperse Blue 9 solutions in 75/25 methanol/water and other solutions which had been diluted less than 10 times before analysis on the spectrophotometer.

It was thought that if a constant amount of absorbance contributed by carbon were subtracted from the maximum absorbance and the absorbance at 675 nm for the dye solution which had been in contact with carbon, then the ratio of the two remainders would give a value close to that of the ratios obtained from the calibration spectra of the

particular dye and solution under consideration.

$$\frac{A_{max} - X}{A_{675} - X} = R_{cal.}$$

A_{max} is the maximum peak absorbance, and A_{675} is the absorbance at 675 nm for the carbon contacted solution. X is the amount of carbon contribution to the absorbance. $R_{cal.}$ is the ratio of maximum absorbance and absorbance at 675 nm for the dye solution without contact with carbon. Rearrangement of the equation gives the following:

$$X = \frac{(R_{cal.})\ A_{675} - A_{max}}{(R_{cal.} - 1)}$$

This equation was used to calculate the contribution of carbon to the absorbance values of dye solutions after contact of the solutions with carbon. This quantity X was subtracted from the maximum absorbance to give the corrected value which was then located on the proper absorbance-concentration plot to give the concentration of the diluted dye solution.

APPENDIX C

PROCEDURES FOR THE PURIFICATION OF DYES

Acid Blue 25

Approximately 20 grams of the commercial dye was dissolved in a minimum amount of N,N-dimethylformamide (approximately 50 ml.). The solution was filtered while hot and a whitish residue containing some blue dye was removed from the solution. The filtered solution was poured into a mixture of 100 ml. of pentane and 70 ml. of xylene. After cooling in ice for about 24 hours the solution was filtered. The dye captured on the filter was washed in pentane and then allowed to dry.

Acid Blue 145

A sample of commercial Acid Blue 145 was extracted with N,N-Dimethylformamide in a soxhlet for about two days. The solution of the dye in dimethylformamide was then evaporated to dryness and the purified dye recovered.

Disperse Blue 9

Two procedures were used in an attempt to purify the Disperse Blue 9. In both procedures the dye was extracted in hot benzene. In one procedure the dye-benzene solution was evaporated to dryness to recover the dye. In the other procedure ethanol and water were added to the dye-benzene solution and an azeotrope of benzene, water and ethanol was distilled off, leaving a solution of the dye in ethanol. The dye solution was cooled and time was allowed for the recrystallization of the dye from ethanol.

APPENDIX D

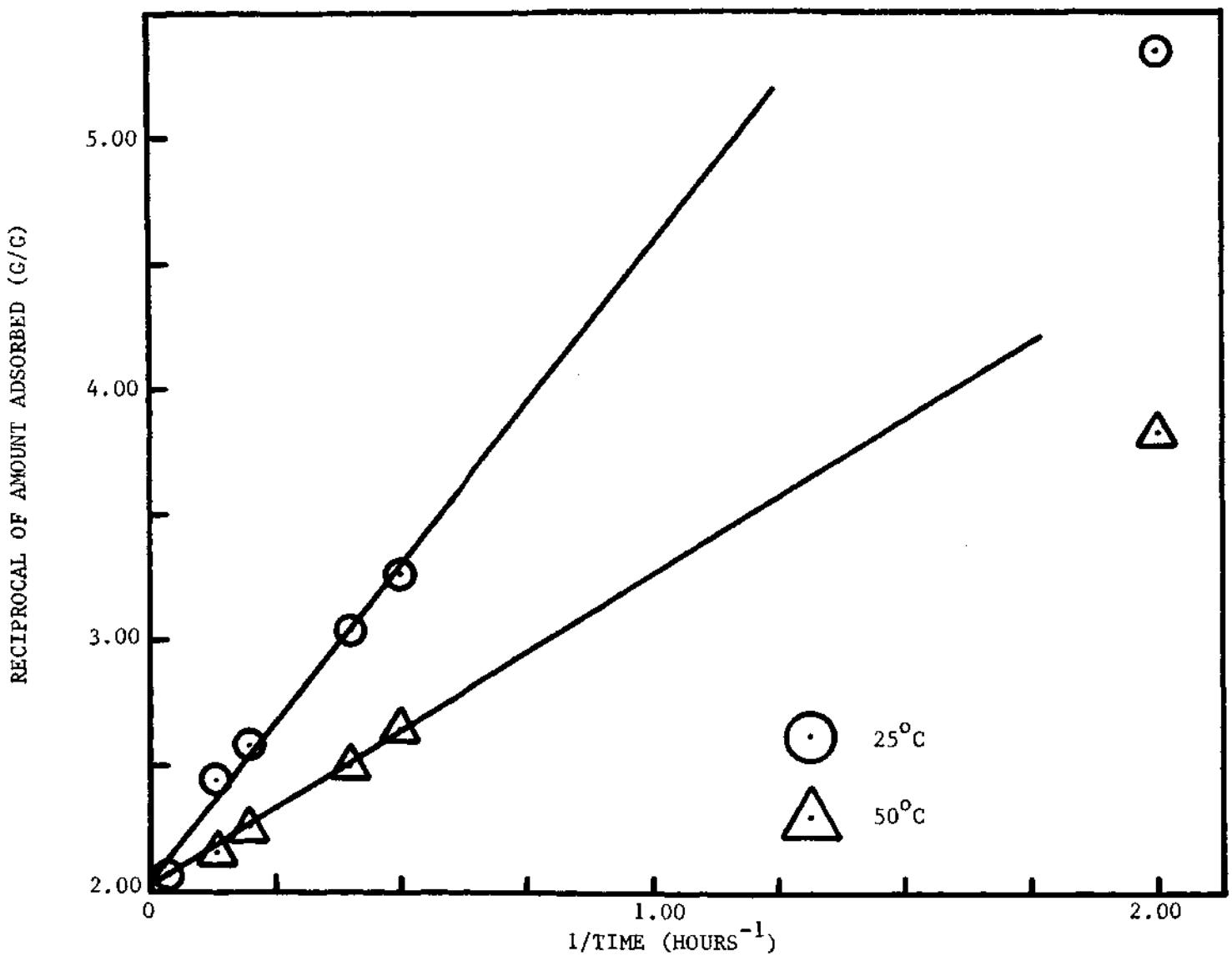


Figure 40. Reciprocal Plot of Adsorption-Time Curves for Impure Acid Blue 25 in Water

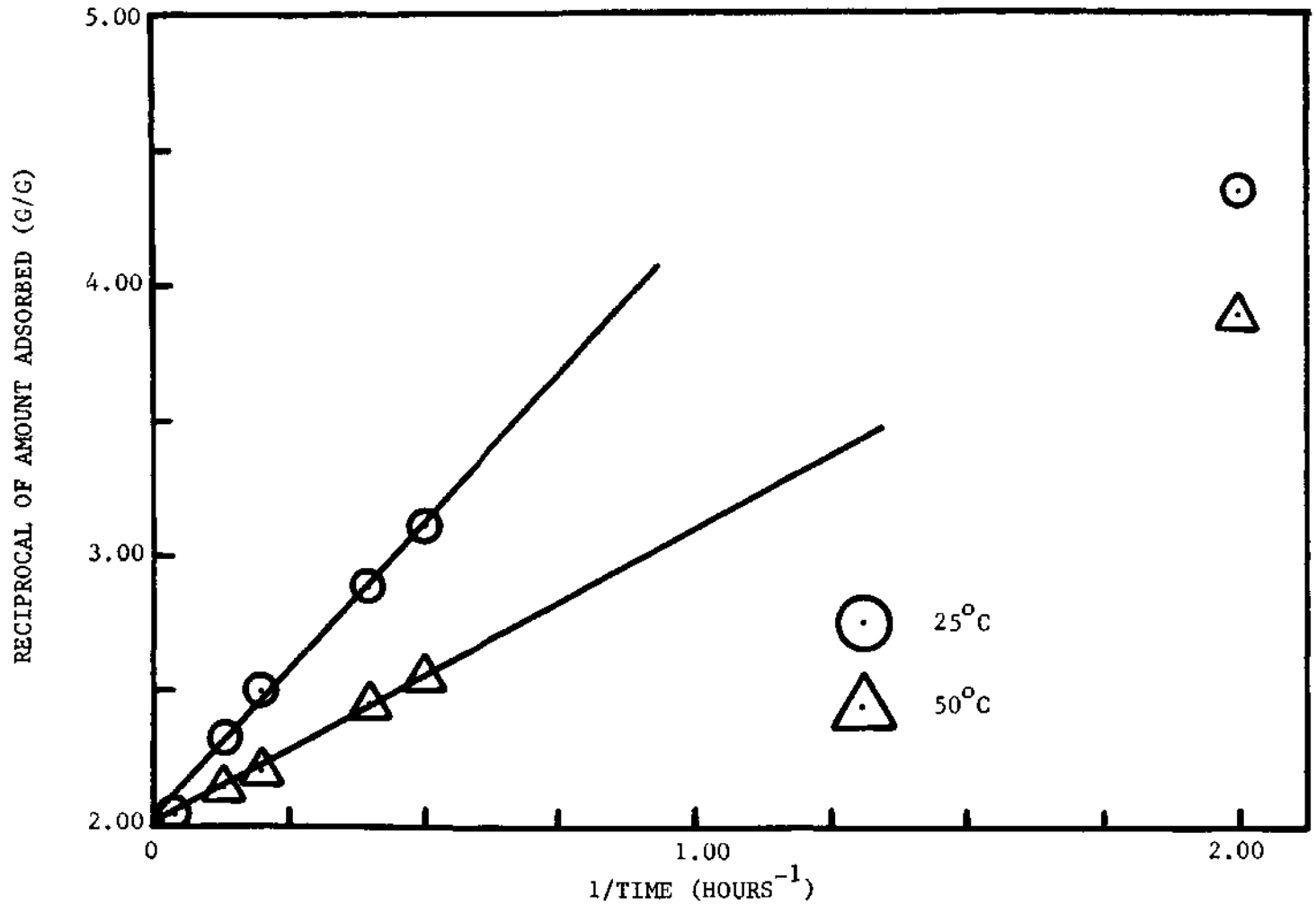


Figure 41. Reciprocal Plot of Adsorption-Time Curves for Impure Acid Blue 145 in Water

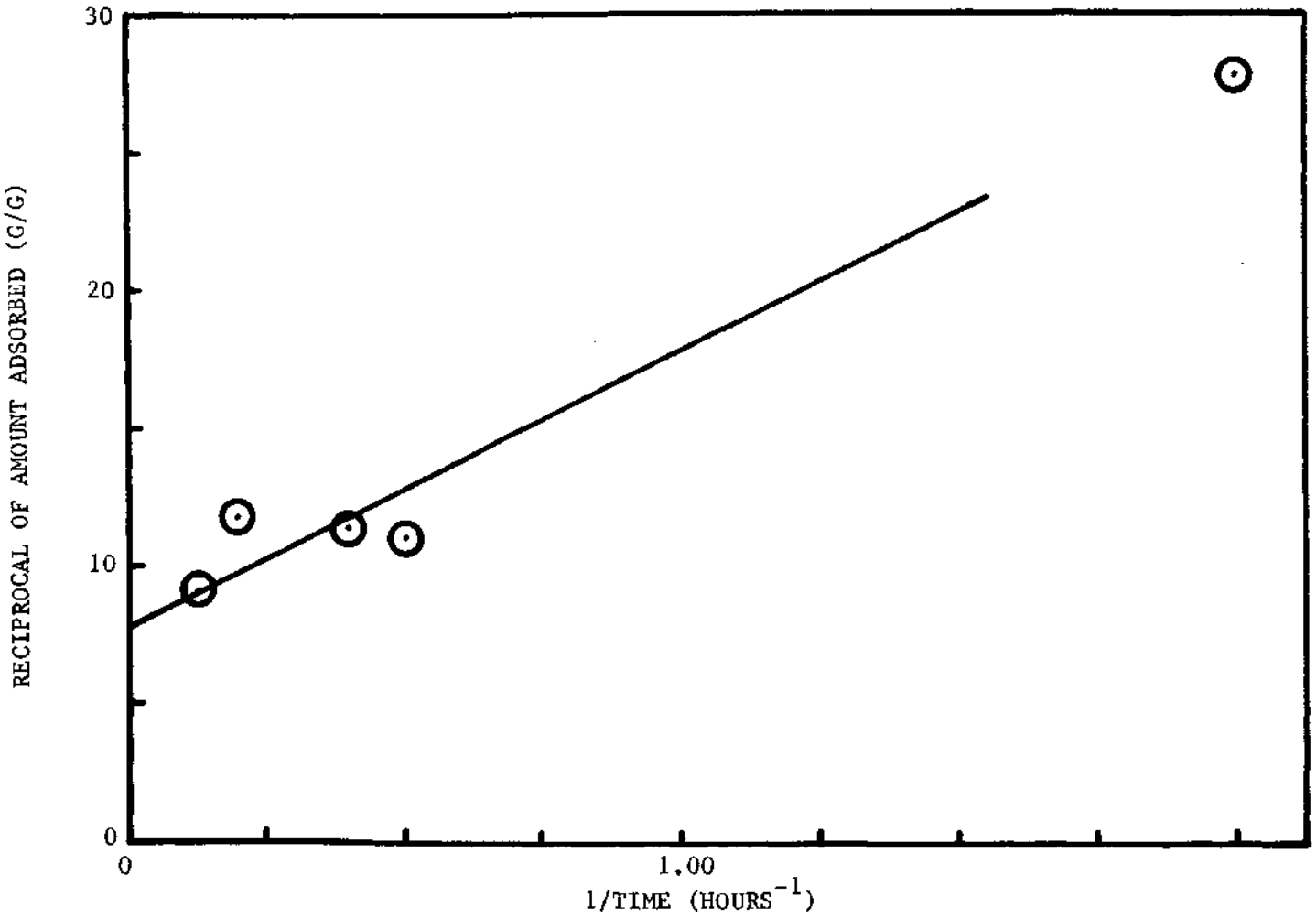


Figure 42. Reciprocal Plot of Adsorption-Time Curve for Impure Disperse Blue 9 in Water

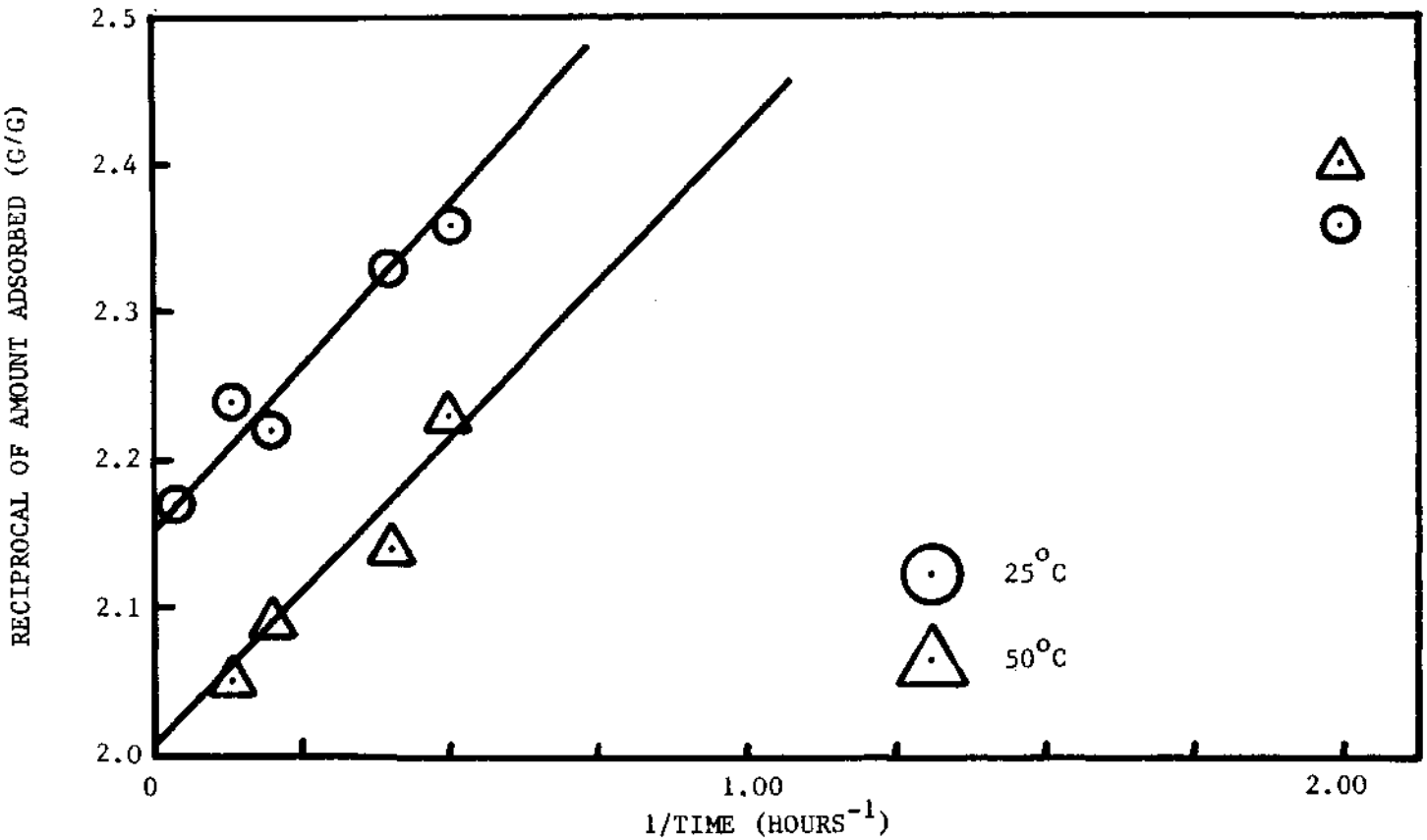


Figure 43. Reciprocal Plot of Adsorption-Time Curves for Impure Disperse Blue 9 in 75/25 Methanol/Water

BIBLIOGRAPHY

1. Porter, J. J., Abernathy, A. R., Ford, J. M., Lyons, D. W., State of the Art of Textile Waste Treatment, Projects Report System, Water Quality Office, Environmental Protection Agency, Washington, D. C., February, 1971.

2. Rodman, Clarke A., "Removal of Color from Textile Dye Wastes" - A paper presented at the Technical Conference of the American Association of Textile Chemists and Colorists in October, 1971.

3. Flege, R. K., "Determination of Degraded Dyes and Auxiliary Chemicals in Effluents from Textile Dyeing Operations", Department of the Interior, Office of Water Resources Research Project Number B-027-6A, A. French Textile School of Georgia Institute of Technology in cooperation with the Environment Resources Center, March, 1970.

4. Shunney, E. L., Perrotti, A. E., Rodman, C. A., "Decolorization of Carpet Yarn Dye Wastewater", American Dyestuff Reporter, June, 1971, 32-40.

5. "Activated Carbon Reclaims Textile Industry's Waste Waters", Environmental Science and Technology, 3, no. 4, 314-315, (1969).

6. Suchecki, S. M., "A Dyer's Operation Cleanup", Textile Industries, 130, 113-126, 136, 175 (1966).

7. Freundlich, H., and Losev, G., "The Adsorption of Dyestuffs by Carbon and by Fibers", Zeitschrift fur Physikalische Chemie, 59, 284-312, (1907). (In German). (Abstract no. 1391 from Deitz, V. R., Bibliography of Solid Adsorbents, United Cane Sugar Refiners and Bone Char Manufacturers, and National Bureau of Standards, Washington, D. C., 1944.)

8. Cerny, S., and Smisek, M., Active Carbon, Elsevier Publishing Company, New York, 1970.

9. Knecht, E., "Decolorizing Action of Various Forms of Charcoal", Journal of the Society of Chemical Industry, 28, 700, (1909).

10. Rohland, P., "The Adsorptive Power of Clays, Kaolins, and Talcs", Apotheker Zeitung, 31, 40-2, (1916). (Bibliography of Solid Adsorbents, no. 1419).

11. Graham, D., "Characterization of Physical Adsorption Systems. III. The Separate Effects of Pore Size and Surface Acidity upon the Adsorbent Capacities of Activated Carbons", Journal of Physical Chemistry, 59, 896-900, (1955).

12. Yajnik, N. A., Goyle, D. N., Das, I., and Jain, J. R., "The Effect of pH on Adsorption from Solution", Kolloid Zeitschrift, 77, 99-103, (1936). (Bibliography of Solid Adsorbents, no. 1603).

13. Sastri, M. V. C., "Adsorption of Methylene Blue by Activated Carbon", Current Science, 7, 228, (1938)

14. Grollman, A., "The Combination of Phenol Red and Proteins", Journal of Biological Chemistry, 64, 141-160, (1925).

15. Bartell, F. E., and Miller, E. J., "Adsorption by Activated Sugar Charcoal", Journal of the American Chemical Society, 45, 1106-1115, (1923).

16. Doss, K. S. G., and Singh, A., "Adsorption of Thymol Blue on Activated Carbon", Journal of Science and Industrial Research, 12B, 79-83, (1953).

17. Hassler, J. W., Activated Carbon, Chemical Publishing Company, Incorporated, New York, 1963.

18. Pincussen, L., "Adsorption Experiments with Various Charcoals", Biochemische Zeitschrift, 137, 117-120, (1923).

19. Rossi, G., and Basini, A., "Adsorption by Animal Charcoal", Annali di Chimica Applicata, 16, 306-313, (1926). (Bibliography of Solid Adsorbents, no. 1467).

20. Pelet-Jolivet, L., and Siegrist, H., "The Adsorption of Methylene Blue and Crystal Ponceau by Carbon and its Dependence on Temperature", Gedenkboek Aangeboden aan J. M. van Bemmelen, 1910, 158-162. (Bibliography of Solid Adsorbents, no. 1402).

21. Hassler, J. W., and McMinn, N. E., "The Nature of Activated Carbon", Industrial and Engineering Chemistry, 37, No. 7, 645-649, (1945).

22. Weber, W. J., and Morris, J. C., "Removal of Biologically Resistant Pollutants from Waste Waters by Adsorption", Advances in Water Pollution Research, 2, 231-266, (1964).

23. Goddard, A. E., and Cooper, E. A., "Adsorption of Aromatic Acids", Chemistry and Industry, July 6, 1957, 952.

24. Porter, J. J., "Concepts for Carbon Adsorption in Waste Treatment", A paper presented at the Seminar on New Developments in Textile Waste Treatment at Clemson University, May 31, - June 4, 1971.

25. Getzen, F. W., and Ward, T. M., "A Model for the Adsorption of Weak Electrolytes on Solids as a Function of pH", Journal of Colloid and Interface Science, 31, 441-453, (1969).